

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

Kiyoko FUJIKI

Department of Agricultural Chemistry, Faculty of Agriculture, Meiji University, Ikuta, Tama-ku, Kawasaki 214

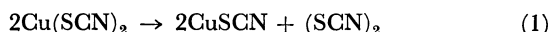
(Received May 20, 1977)

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 (C₆, C₈, and C₁₂).

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⁾

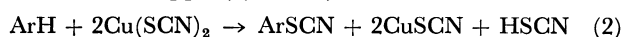
As a means of introducing a thiocyanato group into the aromatic nucleus, thiocyanogen is useful as a reagent for such reactive substrates as amines and phenols.²⁾ Less reactive substrates, such as phenolic ethers, naphthalene derivatives, and anillides, which are unreactive towards thiocyanogen, give thiocyanates in high yields when treated with thiocyanogen chloride in acetic acid;³⁾ however, 2-methoxynaphthalene reacts with not only thiocyanogen chloride³⁾ 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) thiocyanate⁷⁾ 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 method⁹⁾, 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.



Thiocyanation with (SCN)₂ was less reactive in higher alkyl (C₆—C₁₂) naphthyl ethers due to an electrophilic attack of SCN⁺.

To a solution of 1-alkoxynaphthalene in acetic acid we added copper(II) thiocyanate, freshly prepared¹⁰⁾ 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 white²⁾ (actually from black to a yellowish green or yellow color) due to the formation of copper(I) thiocyanate.



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 spectra¹¹⁾ 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 summarized 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 CDCl₃, 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-methoxynaphthalene (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 (CHCl₃) 2145 cm⁻¹ (SCN). NMR (CDCl₃) δ=3.91 (3H, s, OCH₃), 6.72 (1H, d, *J*=7.5 Hz, aromatic proton of the 2-position¹¹⁾), 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 positions¹¹⁾). Found: C, 67.13; H, 3.91; N, 6.55; S, 14.91%; M⁺, 215. Calcd for C₁₂H₉NOS: C, 66.95; H, 4.21; N, 6.51; S, 14.89%; M, 215.

The characterization of other alkoxynaphthyl thiocyanates is as follows. R=C₂H₅, mp 73.5—75 °C. (recrystallization solvent; ethanol. Lit.⁶⁾ bp/7 Torr 105 °C). IR (CHCl₃) 2140 cm⁻¹. NMR (CDCl₃) 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 C₁₃H₁₁NOS; C, 68.10; H, 4.84; N, 6.11; S, 13.98%; M, 229. R=*n*-C₃H₇, mp 82.2—83.5 °C (isopropanol, lit.⁶⁾ bp/4 Torr

TABLE 1. THIOCYANATION OF 1-ALKOXYNAPHTHALENE

R	Alkoxy-naphthalene : Cu(SCN) ₂ (molar ratio)		Temp (°C)	Time (h)	Yield (%)
CH ₃	1	4	67—70	2.5	79.2
C ₂ H ₅	1	4	64—69	2.0	80.8
C ₂ H ₅ ^{a)}	1	2	115—118	5.0	—
<i>n</i> -C ₃ H ₇	1	4	70—76	2.8	67.8
<i>n</i> -C ₄ H ₉	1	4	65—70	2.5	60.3
<i>i</i> -C ₅ H 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
<i>n</i> -C ₆ H ₁₃	1	4	77—79	2.5	38.5
<i>n</i> -C ₈ H ₁₇	1	4	90—92	1.5	19.1
<i>n</i> -C ₁₂ H ₂₅	1	4	77	2.4	24.2

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

109—110 °C). IR (CHCl₃) 2145 cm⁻¹. NMR (CDCl₃) δ = 1.08 (3H, t, *J* = 7 Hz), 1.90 (2H, sex, *J* = 7 Hz), 4.00 (2H, t, *J* = 7 Hz, OCH₂), 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 C₁₄H₁₃NOS: S, 13.18%; M, 243. R = *n*-C₄H₉, mp 50—51.5 °C (methanol, lit.⁶) bp/6 Torr 127—130 °C). IR (CHCl₃) 2140 cm⁻¹. NMR (CDCl₃) 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 C₁₅H₁₅NOS: C, 70.30; H, 5.90; N, 5.65; S, 12.42%; M, 257. R = *iso*-C₅H₁₁, mp 40—41 °C (methanol, lit.⁶) bp/5 Torr 113—116 °C). IR (KBr) 2140 cm⁻¹. NMR (CDCl₃) δ = 1.01 (6H, d, *J* = 6 Hz, (CH₃)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 C₁₆H₁₇NOS: C, 70.82; H, 6.31; N, 5.16; S, 11.81%; M, 271. R = *n*-C₆H₁₃, mp 41 °C (methanol-water). IR (CHCl₃) 2140 cm⁻¹. NMR (CDCl₃) 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 C₁₇H₁₉NOS: C, 71.54; H, 6.71; N, 4.91%; M, 285. R = *n*-C₈H₁₇, mp 44 °C (methanol). IR (KBr) 2140 cm⁻¹. NMR (CDCl₃) 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 C₁₉H₂₃NOS: C, 72.80; H, 7.40; N, 4.47; S, 10.22%; M, 313. R = *n*-C₁₂H₂₅, mp 44.5—45 °C (acetone-methanol). IR (KBr) 2125 cm⁻¹. NMR (CDCl₃) 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 C₂₃H₃₁NOS: 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 (CHCl₃) No characteristic band of νSCN. NMR (CDCl₃) 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 C₂₄H₂₂O₂S₂: C, 70.90; H, 5.46; S, 15.77%; M, 406.

The author is indebted to the Research Laboratories, Tanabe Pharmaceutical Co., Ltd., for the elemental analyses and the obtaining the mass and NMR spectra.

References

- 1) a) Y. Hamada, H. Matsuoka, and H. Fukatsu, *Yakugaku Zasshi*, **91**, 565 (1971); b) A. A. Newman, Ed., "Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives," Academic Press, London (1975), Chap. 4.
- 2) J. L. Wood, *Org. React.*, **3**, 240 (1946).
- 3) R. G. R. Bacon and R. G. Guy, *J. Chem. Soc.*, **1960**, 318.
- 4) N. Kharasch, ed., "Organic Sulfur Compounds," Pergamon Press, Vol. 1, New York (1961), Chap. 27.
- 5) A. Kaji, *Nippon Kagaku Zasshi*, **82**, 382 (1961).
- 6) A. Kaji and S. Kano, Japan Patent 1722 (1962); *Chem. Abstr.*, **58**, 7886g.
- 7) S. Uemura, S. Uchida, M. Okano, and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **46**, 3254 (1973).
- 8) E. C. Taylor, F. Kienzle, and A. McKillop, *Synthesis* **1972**, 38.
- 9) H. P. Kaufmann, "Newer Methods of Preparative Organic Chemistry," Interscience, Vol. 1, New York (1948), pp. 377—379.
- 10) C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, **36**, 3095 (1971).
- 11) G. O. Dudek, *Spectrochim. Acta*, **19**, 691 (1963).
- 12) M. Yokoyama, K. Iwata, and S. Toyoshima, *Yakugaku Zasshi*, **78**, 428 (1958).