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An Efficient *p*-Thiocyanation of Phenols and Naphthols Using a Reagent Combination of Phenyliodine Dichloride and Lead(II) Thiocyanate

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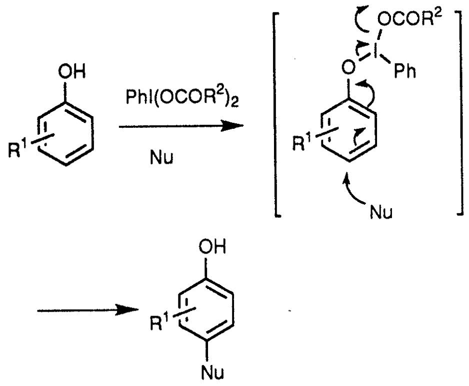
A combination of $PhICl_2$ and $Pb(SCN)_2$ is effective for the *p*-selective thiocyanation of various types of *p*-unsubstituted phenols and naphthols 1 to give *p*-thiocyanatophenols and naphthols 3. The reaction proceeded at 0 °C to room temperature in good to quantitative yields. Twenty-five examples are given, in which various functional groups, such as chloro, allyl, carbonyl, ester, amide, and primary hydroxyl groups, are shown to be compatible with this reaction.

Key words thiocyanation; phenol; hypervalent iodine reagent; lead(II) thiocyanate

Because the thiocyanato group can be transformed into various sulfur functional groups and sulfur-containing heterocycles, the thiocyanation of aromatic compounds is an important subject.[1,2] Many thiocyanation methods have been developed using electrophilic thiocyanato species, generated by the chemical[1] or electrochemical[3] oxidation of thiocyanate anions. The thiocyanation of aromatic amines was reported to occur rapidly to give high yields of the products. On the other hand, the thiocyanation of phenols has not been as extensively studied, and the yields did not appear to be as high as those with aromatic amines. In particular, the presence of electron-withdrawing substituents on the aromatic rings reduced the yields.[1,4–6] In connection with our project on the development of novel transformation reactions of the *p*-sulfinyl group of phenol derivatives through the Pummerer-type reaction,[7] we briefly reported an efficient *p*-thiocyanation of various phenol compounds by using the combination of $PhICl_2$ and $Pb(SCN)_2$.[8] Here we describe this reaction in detail.

Results and Discussion

We reported that hypervalent iodine(III) reagents, phenyliodine diacetate and phenyliodine bis(trifluoroacetate) (PIFA), are useful for the oxidative addition of alcohols, water, and carboxylic acids at the *para*-position of phenols (Chart 1).[9] Similar types of *p*-substitution reactions have been widely reported in the presence of inter- and intramolecular nucleophiles, including amides, oximes, fluoride ion, electron-rich olefins, and electron-rich aromatic compounds.[10] Therefore, we expected that a similar reaction using a reagent combination of a hypervalent iodine(III) compound and a thiocyanate anion ($Nu = {}^{-}SCN$) would be useful for the *p*-thiocyanation of phenols **1**.



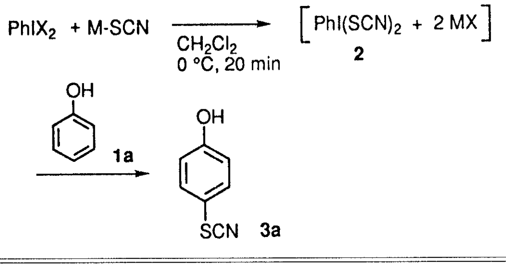
Nu; R^3O, HO, R^3CO_2, $R^3_2C{=}N\text{-}O$, F, $R^3\text{-}CH{=}CH$, Ar, etc.

Chart 1

We anticipated that the appropriate reagent combination of known iodinanes and thiocyanates would undergo ligand-exchange reaction to generate a novel iodinane **2**, suitable for thiocyanation. We preliminarily tried three types of reagent combinations (runs 1—3 in Table 1); however, **2** or related iodinanes having one or two thiocyanato ligands could not be isolated or even characterized by spectroscopic means. The compounds identified by IR and ¹H-NMR spectroscopies were iodobenzene and thiocyanogen, even by rapid measurement of ¹H-NMR data between −78 and 0 °C. However, we found that the addition of phenol **1a** to each reaction mixture immediately gave the *p*-thiocyanatophenol **3a** in high to quantitative yield (Table 1).

For example, under a nitrogen atmosphere, $PhICl_2$ (1.2 mmol) and $Pb(SCN)_2$ (1.5 mmol) were stirred in dry

Table 1. Combination of the Hypervalent Iodine(III) Reagent and the Thiocyanate and Its Reaction with Phenol (**1a**)



Run	$PhIX_2$	M-SCN	Yield (%) of **3a**[a]
1	$PhI(OCOCF_3)_2$	TMS-NCS (2 eq)	95
2	$PhI{=}O$	TMS-NCS (2 eq)	56
3	$PhICl_2$	$Pb(SCN)_2$ (1.2 eq)	93

[a] Isolated yield after SiO_2 chromatography.

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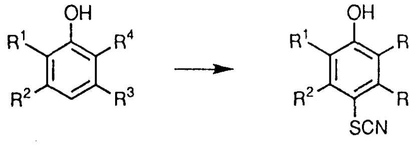
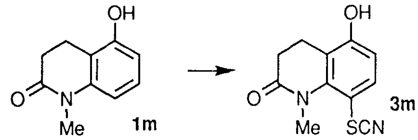
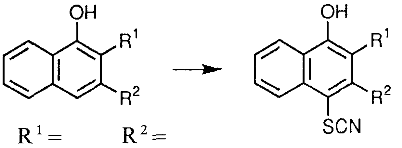
CH_2Cl_2 at 0 °C for 20 min. Phenol **1a** (1.0 mmol) was added to the resultant suspension, and the whole was stirred for 30 min. The reaction mixture was filtered, concentrated, and purified by column chromatography on SiO_2 to give *p*-thiocyanatophenol **3a** in 93% yield (run 3). Similarly, the use of PIFA and TMS–NCS gave 95% yield of **3a** (run 1), while that of iodosobenzene and TMS–NCS was not satisfactory (run 2). Among the former combinations, the use of $PhICl_2$ and $Pb(SCN)_2$ seemed to be favorable to that of PIFA and TMS–NCS because the former two reagents are readily available and easily handled solids.

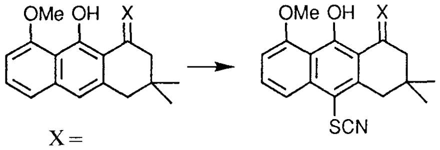
Table 2. Thiocyanation of Various Phenols (**1**) Using $PhICl_2$–$Pb(SCN)_2$



Run	Phenol **1**	R^1=	R^2=	R^3=	R^4=	Product **3**	Yield (%)[a]
1	**1a**	H	H	H	H	**3a**	93
2	**b**	CN	H	H	H	**b**	61
3	**c**	Me	H	H	Me	**c**	78
4	**d**	^{t}Bu	H	H	^{t}Bu	**d**	97
5	**e**	Cl	H	H	Cl	**e**	64
6	**f**	H	Me	Me	H	**f**	95
7	**g**	H	Me	Me	Me	**g**	81
8	**h**	Me	Me	Me	Me	**h**	94
9	**i**	allyl	Me	Me	Me	**i**	79
10	**j**	allyl	Me	Me	allyl	**j**	89
11	**k**	COMe	Me	Me	Me	**k**	78
12	**l**	$(CH_2)_3OH$	Me	Me	Me	**l**	91
13	**1m**					**3m**	65

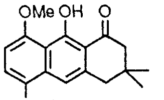


Run	Phenol **1**	R^1=	R^2=	Product **3**	Yield (%)[a]
14	**1n**	H	H	**3n**	88
15	**o**	COMe	H	**o**	97
16	**p**	Me	Me	**p**	67
17	**q**	COMe	Me	**q**	86
18	**r**	COMe	Ph	**r**	85
19	**s**	CO_2Et	Me	**s**	97
20	**t**	CO_2Et	CH_2OCOMe	**t**	88
21	**u**	CO_2Et	CO_2Et	**u**	58
22	**v**	$CONEt_2$	Me	**v**	98
23	**w**	$CONEt_2$	$CONEt_2$	**w**	91



Run	Phenol **1**	X=	Product **3**	Yield (%)[a]
24	**1x**	H_2	**3x**	94
25	**y**	O	**y**	61[b]

a) Isolated yield after SiO_2 chromatography. *b*) The by-product **4** was isolated.

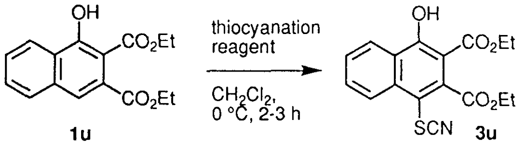


4 (18%)

Using this method, various phenols, **1b**—**m**, and naphthols, **1n**—**y**, were thiocyanated to give the corresponding products **3b**—**y**. The results are summarized in Table 2. Several features are noteworthy. i) Usually the reaction was completed at 0 °C within 1 h. ii) In most cases, the reaction exclusively occurred at the *para*-position of the phenol ring when the *para*-position was free.[11] Even in the cases of 3,5-dimethylphenol **1f** and the congested tricyclic naphthol **1x**, the *p*-thiocyanates **3f**, **x** were obtained as single products in excellent yields (runs 6, 24). However, the similar reaction of the oxo-tricyclic naphthol **1y** was not regiospecific, giving a mixture of the *p*-thiocyanate **3y** (61%) and its regio isomer **4** (18%) (run 25). iii) All products were thiocyanates (**3a**—**y**, **4**), and the corresponding isothiocyanates were not obtained at all. The structures were determined from the IR absorption spectra, because the products showed IR absorptions at 2172—2151 cm^{-1}, while those of the isothiocyanates are reported to be in the range of 2140—1990 cm^{-1}. iv) Reactive functional groups such as allyl and primary hydroxyl groups were compatible (runs 9, 10, 12). v) The phenols having electron-withdrawing cyano, chloro, carbonyl, ester, and amido groups were converted to the corresponding thiocyanates **3b**, **e**, **k**, **o**, **q**—**w**, and **y** in good yields (runs 2, 5, 11, 15, 17—23, 25). However, *o*-nitrophenol did not react even when the reaction mixture was stirred at room temperature for 1 d.

As we previously mentioned, spectroscopic measurement of the ligand-exchange reaction of $PhICl_2$ and $Pb(SCN)_2$ revealed complete formation of iodobenzene and thiocyanogen. However, a comparative examination of our reagent system (run 1 in Table 3) with the ordinary method using thiocyanogen (run 3) revealed that the former was more effective than the latter. The addition of PhI to the reaction mixture of run 3 slightly increased the yield of **3u** (runs 4, 6). These results may suggest that there is an equilibrium between the novel iodinane **2** and the mixture of iodobenzene and thiocyanogen lying far to the right (Chart 2) and that **2** takes part in the thiocyanation

Table 3. Thiocyanation of **1u** under Various Conditions



Run	Thiocyanation reagent	Yield (%) of **3u**[a]
1	$PhICl_2$ (1.2 eq), $Pb(SCN)_2$ (1.5 eq)	58
2	$PhICl_2$ (2 eq), $Pb(SCN)_2$ (3 eq)[b]	44
3	$(SCN)_2$[c] (2 eq)	30
4	$(SCN)_2$[c] (2 eq), PhI (2 eq)	40
5	$(SCN)_2$[c] (2 eq), $PbCl_2$ (2 eq)	39
6	$(SCN)_2$[c] (2 eq), PhI (2 eq), $PbCl_2$ (2 eq)	45

a) Isolated yield after SiO_2 chromatography. *b*) Run after filtration of the by-product, $PbCl_2$. *c*) Generated from bromine and $Pb(SCN)_2$ in CH_2Cl_2 at 0 °C for 20 min and used after filtration of the by-product, $PbBr_2$.

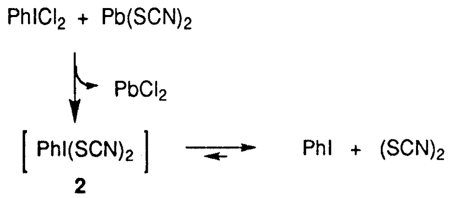


Chart 2

as a reactive molecule. The presence of a weak Lewis acid, $PbCl_2$, seems to accelerate the reaction, because removal of $PbCl_2$ from the reaction mixture of run 1 decreased the yield of **3u** (run 2), while addition of $PbCl_2$ increased the yield (runs 5, 6).

Although elucidation of the reaction mechanism would require a more detailed study, it is clear that the use of the mixture of $PhICl_2$ and $Pb(SCN)_2$ without filtration of the by-product $PbCl_2$ provides a convenient thiocyanation of phenols.[12-15] This method features i) good to high yields of the products from various types of phenols having electron-withdrawing groups and other reactive functional groups, ii) exclusive *para*-selectivity, and iii) an easy procedure using solid and stable $PhICl_2$ and $Pb(SCN)_2$.

Experimental

All melting points are uncorrected. IR absorption spectra were recorded on a Shimazu FT-IR-8100 spectrometer by diffuse reflectance measurement of samples dispersed in KBr powder. ^{1}H-NMR spectra were recorded on Varian VXR-200 (200 MHz), Hitachi R-250HT (250 MHz), and JEOL JNM-EX270 (270 MHz) spectrometers with $SiMe_4$ as an internal standard. High-resolution mass spectra (HR-MS) were recorded at 70 eV with a direct inlet system on JEOL JMS-D300 and JEOL JMS-HX100 spectrometers. E. Merck Silica gel 60 (70-230 mesh ASTM) was used for column chromatography. Phenyliodine(III) dichloride was prepared according to the reported procedure.[16] $Pb(SCN)_2$ was a commercial product, used as supplied.

General Procedure for the Thiocyanation of Phenols (1) Under a nitrogen atmosphere, $PhICl_2$ (330 mg, 1.2 mmol) was added to an ice-cooled suspension of $Pb(SCN)_2$ (485 mg, 1.5 mmol) in dry CH_2Cl_2 (10 ml). The reaction mixture was stirred at the same temperature for 20 min, then a solution of the phenol **1** (1.0 mmol) in dry CH_2Cl_2 (2 ml) was added. The whole was stirred for 30 min, filtered through a Celite pad, and concentrated to half volume. Silica gel (2 g) for column chromatography was added, and the solvent was evaporated *in vacuo*. The product absorbed on SiO_2 was charged on an SiO_2 column and eluted with AcOEt–hexane to give the *p*-thiocyanatophenol **3**. The yields are summarized in Table 2.

4-Thiocyanatophenol (**3a**): Colorless crystals. mp 59—60 °C (AcOEt–hexane) (lit.[13] mp 59—60 °C). IR 3350, 2161, 1599, 1584, 1497 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 5.69 (1H, br s), 6.88 (2H, d, J=9.5 Hz), 7.45 (2H, d, J=9.5 Hz).

2-Cyano-4-thiocyanatophenol (**3b**): Colorless crystals. mp 140—145 °C (CH_2Cl_2). IR 3250, 2230, 2172, 1597, 1493 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.02 (1H, d, J=9.0 Hz), 7.63 (1H, dd, J=2.5, 9.0 Hz), 7.72 (1H, d, J=2.5 Hz). HR-MS Calcd for $C_8H_4N_2OS$: 176.0044. Found 176.0044.

2,6-Dimethyl-4-thiocyanatophenol (**3c**): Colorless crystals. mp 103.5—104 °C (CH_2Cl_2–hexane) (lit.[17] mp 100—101 °C). IR 3450, 2155, 1584, 1480 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.26 (6H, s), 4.90 (1H, s), 7.21 (2H, s).

2,6-Di-*tert*-butyl-4-thiocyanatophenol (**3d**): Colorless crystals. mp 54—55 °C (pentane) [lit.[18] mp 64—66.5 °C (pentane)]. IR 3629, 2157, 1428 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.44 (18H, s), 5.50 (1H, br s), 7.37 (2H, s).

2,6-Dichloro-4-thiocyanatophenol (**3e**): Colorless crystals. mp 101—102 °C (CH_2Cl_2–hexane). IR 3299, 2172, 1563, 1478, 1460 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 6.17 (1H, br s), 7.53 (2H, s). *Anal.* Calcd for $C_7H_3Cl_2NOS$: C, 38.20; H, 1.37; N, 6.36. Found: C, 38.24; H, 1.56; N, 6.32.

3,5-Dimethyl-4-thiocyanatophenol (**3f**): Colorless crystals. mp 132—133 °C (CH_2Cl_2–hexane) (lit.[17] mp 127—129 °C). IR 3347, 2159, 1588, 1458 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.54 (6H, s), 6.66 (2H, s).

2,3,5-Trimethyl-4-thiocyanatophenol (**3g**): Colorless crystals. mp 161—162 °C (CH_2Cl_2–hexane). IR 3400—3100 br, 2166, 1582 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.17 (3H, s), 2.50 (3H, s), 2.55 (3H, s), 5.33 (1H, br s), 6.62 (1H, s). *Anal.* Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25; S, 16.59. Found: C, 62.02; H, 5.73; N, 7.22; S, 16.59.

2,3,5,6-Tetramethyl-4-thiocyanatophenol (**3h**): Colorless crystals. mp 146.5—147 °C (CH_2Cl_2–hexane) [lit.[19] mp 144.5—145 °C (Et_2O)]. IR 3415, 2163, 1561 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.21 (6H, s), 2.57 (6H, s), 5.03 (1H, s).

2-Allyl-3,5,6-trimethyl-4-thiocyanatophenol (**3i**): Colorless crystals. mp 93—93.5 °C (CH_2Cl_2–hexane). IR 3450, 2153, 1638, 1550, 1449, 1402 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.21 (3H, s), 2.58 (6H, s), 3.46 (2H, d, J=4.0 Hz), 5.02 (1H, d, J=18.0 Hz), 5.13 (1H, d, J=10.0 Hz), 5.19 (1H, s), 5.84—6.06 (1H, m). *Anal.* Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.48; N, 6.00; S, 13.74. Found: C, 66.81; H, 6.30; N, 5.98; S, 13.58.

2,6-Diallyl-3,5-dimethyl-4-thiocyanatophenol (**3j**): Colorless crystals. mp 95—97 °C (AcOEt–hexane). IR 3420, 2164, 1553 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.58 (6H, s), 3.47 (4H, br d, J=5.5 Hz), 5.00 (2H, dd, J=2.0, 18.0 Hz), 5.11 (2H, dd, J=1.5, 10.0 Hz), 5.29 (1H, s), 5.86—6.01 (2H, m). *Anal.* Calcd for $C_{15}H_{17}NOS$: C, 69.49; H, 6.61; N, 5.40; S, 12.36. Found: C, 69.22; H, 6.60; N, 5.33; S, 12.19.

2-Acetyl-3,5,6-trimethyl-4-thiocyanatophenol (**3k**): Colorless crystals. mp 59.5—60 °C (CH_2Cl_2–hexane). IR 3400, 2153, 1697, 1626, 1582, 1559 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.22 (3H, s), 2.61 (3H, s), 2.64 (3H, s), 2.82 (3H, s), 11.80 (1H, s). *Anal.* Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95; S, 13.63. Found: C, 61.21; H, 5.50; N, 5.93; S, 13.39.

2-(3-Hydroxypropyl)-3,5,6-trimethyl-4-thiocyanatophenol (**3l**): Colorless crystals. mp 91—92 °C (CH_2Cl_2–hexane). IR 3700—3100 br, 2153, 1557 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.84 (2H, tt, J=5.5, 6.5 Hz), 2.20 (3H, s), 2.54 (3H, s), 2.56 (3H, s), 2.82 (2H, t, J=6.5 Hz), 2.92 (1H, br s), 3.59 (2H, t, J=5.5 Hz), 7.95 (1H, br s). HR-MS Calcd for $C_{13}H_{17}NO_2S$: 251.0980. Found 251.0986.

5-Hydroxy-1-methyl-8-thiocyanato-3,4-dihydroquinolin-2(1*H*)-one (**3m**): Colorless crystals. mp 175—177 °C (CH_2Cl_2–hexane). IR 3250, 2205, 1650, 1609 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.65 (1H, d, J=7.0 Hz), 2.70 (1H, d, J=6.0 Hz), 2.98 (1H, d, J=6.0 Hz), 3.03 (1H, d, J=7.0 Hz), 3.36 (3H, s), 6.78 (1H, d, J=9.0 Hz), 7.13 (1H, d, J=9.0 Hz). HR-MS Calcd for $C_{11}H_{10}N_2O_2S$: 234.0460. Found 234.0460.

4-Thiocyanato-1-naphthol (**3n**): Colorless crystals. mp 112.5—113 °C (CH_2Cl_2–hexane) (lit.[4a)] mp 112—113 °C). IR 3300, 2161, 1592, 1570, 1514 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 6.03 (1H, s), 6.81 (1H, d, J=8.0 Hz), 7.60 (1H, t, J=8.0 Hz), 7.73 (1H, t, J=8.0 Hz), 7.75 (1H, d, J=8.0 Hz), 8.29 (2H, d, J=8.0 Hz).

2-Acetyl-4-thiocyanato-1-naphthol (**3o**): Colorless crystals. mp 160—161 °C (CH_2Cl_2–hexane). IR 3069, 2155, 1622, 1590, 1568, 1501 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.72 (3H, s), 7.67 (1H, t, J=7.5 Hz), 7.86 (1H, t, J=7.5 Hz), 8.14 (1H, s), 8.26 (1H, d, J=8.5 Hz), 8.54 (1H, d, J=8.5 Hz). *Anal.* Calcd for $C_{13}H_9NO_2S$: C, 64.18; H, 3.73; N, 5.76; S, 13.18. Found: C, 64.12; H, 3.85; N, 5.75; S, 13.14.

2,3-Dimethyl-4-thiocyanato-1-naphthol (**3p**): Colorless crystals. mp 150—153 °C (AcOEt–hexane) [lit.[19] mp 151—153 °C (ligroin)]. IR 3750, 2145, 1592, 1557, 1499 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.38 (3H, s), 2.80 (3H, s), 5.56 (1H, s), 7.53 (1H, t, J=8.0 Hz), 7.65 (1H, t, J=8.0 Hz), 8.14 (1H, d, J=8.0 Hz), 8.44 (1H, d, J=8.0 Hz).

2-Acetyl-3-methyl-4-thiocyanato-1-naphthol (**3q**): Colorless crystals. mp 122—123 °C (CH_2Cl_2–hexane). IR 3200—2200 br, 2153, 1615, 1572 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.73 (3H, s), 3.02 (3H, s), 7.60 (1H, t, J=8.0 Hz), 7.81 (1H, t, J=8.0 Hz), 8.47 (1H, d, J=8.0 Hz), 8.51 (1H, d, J=8.0 Hz), 13.90 (1H, s). *Anal.* Calcd for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44; S, 12.44. Found: C, 65.16; H, 4.41; N, 5.38; S, 12.44.

2-Acetyl-3-phenyl-4-thiocyanato-1-naphthol (**3r**): Colorless crystals. mp 195—197 °C (CH_2Cl_2–hexane). IR 3200—2100 br, 2153, 1615, 1566 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.78 (3H, s), 7.37—7.39 (2H, m), 7.54—7.55 (3H, m), 7.69 (1H, ddd, J=1.0, 7.5, 8.0 Hz), 7.91 (1H, ddd, J=1.0, 7.5, 8.0 Hz), 8.47 (1H, d, J=8.0 Hz), 8.62 (1H, d, J=8.0 Hz), 14.61 (1H, s). *Anal.* Calcd for $C_{19}H_{13}NO_2S$: C, 71.45; H, 4.10; N, 4.39; S, 10.04. Found: C, 71.25; H, 4.13; N, 4.35; S, 9.95.

2-Ethoxycarbonyl-3-methyl-4-thiocyanato-1-naphthol (**3s**): Colorless crystals. mp 134—135 °C (CH_2Cl_2–hexane). IR 3200—2500 br, 2157, 1653, 1617, 1570 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.48 (3H, t, J=7.0 Hz), 3.02 (3H, s), 4.52 (2H, q, J=7.0 Hz), 7.57 (1H, t, J=8.0 Hz), 7.78 (1H, t, J=8.0 Hz), 8.40 (1H, d, J=8.0 Hz), 8.45 (1H, d, J=8.0 Hz), 12.93 (1H, s). HR-MS Calcd for $C_{15}H_{13}NO_3S$: 287.0613. Found 287.0608.

3-Acetoxymethyl-2-ethoxycarbonyl-4-thiocyanato-1-naphthol (**3t**): Colorless crystals. mp 118—119 °C (CH_2Cl_2–hexane). IR 2157, 1741, 1655, 1619, 1570, 1493 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.44 (3H, t, $J=7.5$ Hz), 2.10 (3H, s), 4.50 (2H, q, $J=7.5$ Hz), 5.91 (2H, s), 7.68 (1H, t, $J=8.0$ Hz), 7.87 (1H, t, $J=8.0$ Hz), 8.49 (1H, d, $J=8.0$ Hz), 8.52 (1H, d, $J=8.0$ Hz), 12.75 (1H, s). *Anal.* Calcd for $C_{17}H_{15}NO_5S$: C, 59.12; H, 4.38; N, 4.06; S, 9.28. Found: C, 59.04; H, 4.39; N, 4.09; S, 9.18.

2,3-Bis(ethoxycarbonyl)-4-thiocyanato-1-naphthol (**3u**): Colorless crystals. mp 125.5—126 °C (CH_2Cl_2–hexane). IR 2159, 1740, 1665, 1619, 1493 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.43 (3H, t, $J=7.5$ Hz), 1.50 (3H, t, $J=7.0$ Hz), 4.42—4.58 (4H, m), 7.71 (1H, t, $J=8.0$ Hz), 7.90 (1H, t, $J=8.0$ Hz), 8.43 (1H, d, $J=8.0$ Hz), 8.54 (1H, d, $J=8.0$ Hz), 13.04 (1H, s). *Anal.* Calcd for $C_{17}H_{15}NO_5S$: C, 59.12; H, 4.38; N, 4.06; S, 9.28. Found: C, 59.38; H, 4.50; N, 3.97; S, 9.16.

2-(*N*,*N*-Diethylcarbamoyl)-3-methyl-4-thiocyanato-1-naphthol (**3v**): Colorless crystals. mp 171—173 °C (CH_2Cl_2–hexane). IR 3000—2900 br, 2153, 1593 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.81—1.50 (6H, m), 2.44 (3H, s), 2.92—4.02 (4H, m), 7.37 (1H, dd, $J=7.0$, 7.5 Hz), 7.50 (1H, dd, $J=7.0$, 7.5 Hz), 7.90—7.94 (2H, m), 10.37 (1H, s). *Anal.* Calcd for $C_{17}H_{18}N_2O_2S$: C, 64.94; H, 5.77; N, 8.91; S, 10.20. Found: C, 64.99; H, 5.84; N, 8.90; S, 10.19.

2,3-Bis(*N*,*N*-diethylcarbamoyl)-4-thiocyanato-1-naphthol (**3w**): Colorless crystals. mp 170—173.5 °C (CH_2Cl_2–hexane). IR 2157, 1636, 1617, 1599, 1576, 1561, 1487 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.07 (3H, t, $J=7.5$ Hz), 1.23—1.36 (9H, m), 3.05—3.93 (8H, m), 7.36 (1H, t, $J=8.0$ Hz), 7.55 (1H, t, $J=8.0$ Hz), 7.71 (1H, d, $J=8.0$ Hz), 8.18 (1H, d, $J=8.0$ Hz), 9.92 (1H, br s). *Anal.* Calcd for $C_{21}H_{25}N_3O_3S$: C, 63.13; H, 6.31; N, 10.52; S, 8.03. Found: C, 63.20; H, 6.33; N, 10.35; S, 8.07.

9-Hydroxy-8-methoxy-3,3-dimethyl-10-thiocyanato-1,2,3,4-tetrahydroanthracene (**3x**): Colorless crystals. mp 155—156 °C (AcOEt–hexane). IR 3400—3300 br, 2151, 1620, 1603, 1561, 1374, 1354 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.06 (6H, s), 1.65 (2H, t, $J=7.0$ Hz), 2.85 (2H, t, $J=7.0$ Hz), 3.01 (2H, s), 4.09 (3H, s), 6.84 (1H, d, $J=8.0$ Hz), 7.45 (1H, t, $J=8.0$ Hz), 8.10 (1H, d, $J=8.0$ Hz), 10.13 (1H, s). HR-MS Calcd for $C_{18}H_{19}NO_2S$: 313.1136. Found 313.1148.

9-Hydroxy-8-methoxy-3,3-dimethyl-10-thiocyanato-1,2,3,4-tetrahydroanthracen-1-one (**3y**): Yellow crystals. mp 142—145 °C (CH_2Cl_2–hexane). IR 2957, 2153, 1615, 1576 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.16 (6H, s), 2.64 (2H, s), 3.29 (2H, s), 4.05 (3H, s), 6.99 (1H, d, $J=8.0$ Hz), 7.73 (1H, t, $J=8.0$ Hz), 8.06 (1H, d, $J=8.0$ Hz), 15.89 (1H, s). HR-MS Calcd for $C_{18}H_{17}NO_3S$: 327.0929. Found 327.0930.

9-Hydroxy-8-methoxy-3,3-dimethyl-5-thiocyanato-1,2,3,4-tetrahydroanthracen-1-one (**4**): Yellow crystals. mp 184—187 °C (CH_2Cl_2–hexane). IR 2950, 2161, 1620, 1565, 1372, 1281, 1107 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.12 (6H, s), 2.62 (2H, s), 2.97 (2H, s), 4.06 (3H, s), 6.82 (1H, d, $J=8.5$ Hz), 7.49 (1H, s), 7.95 (1H, d, $J=8.5$ Hz), 15.12 (1H, s). HR-MS Calcd for $C_{18}H_{17}NO_3S$: 327.0929. Found 327.0932.

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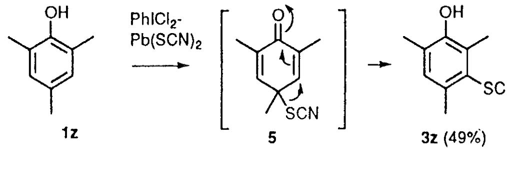
11) The similar reaction of 2,4,6-trimethylphenol **1z** gave the 3-thiocyanatophenol **3z** in 49% yield, probably through migration of the thiocyanato group from the initial product **5**.



12) Use of an equimolar mixture of $PhICl_2$ and $Pb(SCN)_2$ for the thiocyanation of phenols and anilines was briefly reported by Neu in 1939.[13] He used the filtrate of a mixture of $PhICl_2$ and $Pb(SCN)_2$, and the reported yields of the products were not satisfactory. This was probably due to the sensitivity of $PhI(SCN)_2$ to moisture and/or oxygen. Direct addition of phenols to the mixture without the filtration process in our method afforded *p*-thiocyanatophenols in good to quantitative yields.

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