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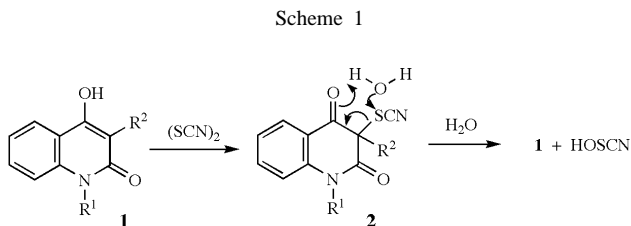
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Under mild reaction conditions, the thiocyanato group is selectively transferred from 1-methyl-3-phenyl-3-thiocyanato-1*H*,3*H*-quinoline-2,4-dione (**3**) to some nucleophiles. Aliphatic primary and secondary amines are converted to *S*-cyanothiohydroxylamines, anilines afford *p*-thiocyanatoanilines, Wittig reagent is thiocyanated in  $\alpha$ -position, and thiols are oxidized to disulfides.

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Reactions of 4-hydroxy-1*H*-quinolin-2-ones (**1**) with thiocyanogen in acetic acid have recently been described [1]. Thiocyanation of **1** proceeds quickly and almost quantitatively to give substituted 3-thiocyanato-1*H*,3*H*-quinoline-2,4-diones (**2**). Compounds **2** are stable in crystalline form but easily transform in protic solvents through a nucleophilic attack by water on the “positively charged” sulfur atom into starting compounds **1** (Scheme 1). Transformation of **2** into **1** has an analogy in reactions of  $\alpha$ -thiocyanato- $\beta$ -diketones with aqueous alkali or with ammonia during which hydrolysis of the thiocyanato group to sulfanyl group does not occur whereas its splitting-off from the molecule does [2,3].



Thiocyanates play an important role in various fields of organosulfur chemistry [4], the thiocyanato group appears in a number of biologically active natural products [5], and thiocyanates are also important starting compounds for synthesizing heterocyclic compounds [6,7]. Study of their reactivity, therefore, is always relevant. The ease with which **2** transformed into **1** as mentioned above inspired us to conceive that compounds of type **2** might also analogously react with other nucleophiles than merely water and thus become versatile thiocyanating agents. Apart from thiocyanogen, which is the oldest but hitherto currently employed thiocyanating agent, whether applied prepared in advance or generated in reaction mixture [8], there are a number of milder and more selective thiocyanating agents described in literature. Thus *N*-thiocyanatosuccinimide was successfully used for electrophilic thiocyanation of reactive arenes and heterocycles [9,10],  $\alpha$ -thiocyanation of enolizable carbonyl compounds was performed with thio-

cyanotrimethylsilane and sulfuryl chloride [11], a mixture of (dichloriodo)benzene - lead(II) thiocyanate was applied to  $\alpha$ -thiocyanation of carbonyl compounds and their silyl enolethers and of  $\alpha$ -dicarbonyl compounds [12], and 4-chloro-5*H*-1,2,3-dithiazol-5-one proved efficient for  $\alpha$ -thiocyanation of  $\alpha$ , $\beta$ -unsaturated  $\alpha$ -aminoesters [13].

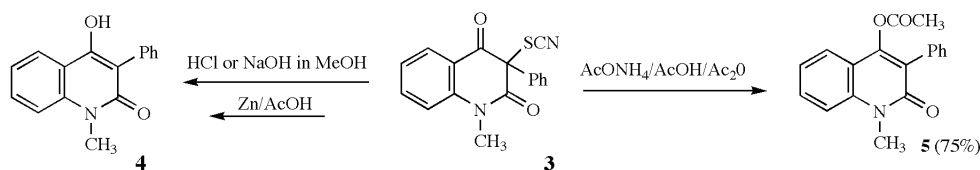
In this paper, we would like to describe the reactions of 1-methyl-3-phenyl-3-thiocyanato-1*H*,3*H*-quinoline-2,4-dione (**3**) with various nucleophiles, as are aliphatic amines, anilines, phenols, thiols, and Wittig reagents.

#### Results and Discussion.

The compounds chosen for studying thiocyanation reactions of various nucleophiles was 1-methyl-3-phenyl-3-thiocyanato-1*H*,3*H*-quinoline-2,4-dione (**3**), which can be easily prepared [1] and is well soluble in organic solvents. On the other hand, 4-hydroxy-1-methyl-3-phenyl-1*H*-quinolin-2-one (**4**), which forms through its transformation, is poorly soluble in benzene as well as in chloroform, which facilitates isolating the main reaction product. Compound **3** is also quite stable – in a methanol solution, for instance, it does not undergo change at room temperature even after several hours; on addition of hydrochloric acid or sodium hydroxide it speedily transforms into compound **4**. Compound **3** does not change in a solution of acetic acid even under boiling. After an addition of acetic anhydride to this solution no changes occur even after 1-hour boiling, but after subsequent addition of solid ammonium acetate and following boiling for an hour, 4-acetoxy-1-methyl-3-phenyl-1*H*-quinolin-2-one (**5**) is produced (Scheme 2). Compound **3** is also readily reduced with zinc in a solution of acetic acid giving rise to **4**. An attempt at thermally initiated isomerization of **3** in boiling cyclohexylbenzene, analogous to rearrangement of 3-hydroxy-1*H*,3*H*-quinoline-2,4-diones [14], was unsuccessful.

Reactions of reagent **3** with nucleophiles were performed in a solution of benzene or chloroform. Compound **3** reacts with aliphatic amines in such manner that a transfer of thiocyanato group to amino group takes place. We thus prepared *S*-cyanothiohydroxylamines **6** and **7** (Chart) in good yields from corresponding benzylamines.

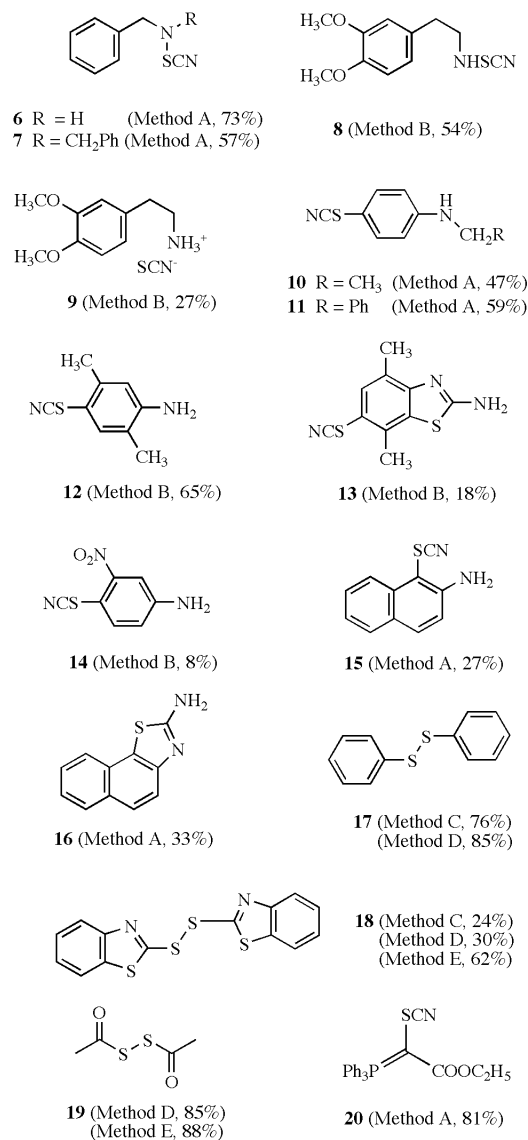
Scheme 2



Conversion of 2-(3,4-dimethoxyphenyl)ethylamine into *N*-thiocyanato derivative **8** indicates high reaction selectivity because the action of thiocyanogen chloride on 2-(3,4-dimethoxyphenyl)ethylamine effect substitution in aromatic ring with formation of 2-(2-thiocyanato-3,4-dimethoxyphenyl)ethylamine hydrochloride [15]. The structure of compound **8** was reliably confirmed by means of 2D nmr experiment. Compound **8**, as opposed to compounds **6** and **7**, is quite unstable and changes in time into quaternary salt **9** and a yellow compound of polymeric character. This change partly occurs even during chromatography of the crude reaction mixture on silica gel column. The total conversion of starting compound to **8** and **9** was 81%. *S*-Cyanothiohydroxylamines have already been known since 1928 [16] but have not yet found use in organic synthesis. Only *S*-cyano-*N*-methylthiohydroxylamine was used to prepare 3,4-dimethyl-5-phenyl-3*H*-thiazol-2-ylideneamine from 1-phenylpropan-2-one [17].

Anilines react with reagent **3** in a different manner than aliphatic amines. The thiocyanato group always enters into *p*-position of the aromatic nucleus producing aromatic thiocyanates. Reaction of **3** with *N*-ethylaniline and *N*-benzylaniline produced *p*-thiocyanatoanilines **10** and **11**. 2,5-Dimethylaniline, which has a more highly activated benzene nucleus, yields expected 4-thiocyanato derivative **12**. However, formation of a disubstituted derivative also takes place to a small extent, and this immediately transforms into corresponding benzothiazole derivative **13**. The total conversion of starting 2,5-dimethylaniline to **12** and **13** was 83%. The predominant or exclusive *p*-orientation in thiocyanation of anilines, known during action of thiocyanogen [8], thus shows up even under action of reagent **3**. This is evident in the result of reaction of **3** with 3-nitroaniline, which has a deactivated benzene nucleus. In spite of that it yields, even though to a minor extent, compound **14**. If *p*-position is occupied, as is the case with 4-nitroaniline, a reaction does not proceed even after a boiling of several hours. When reacting compound **3** with 2-naphtylamine, the anticipated thiocyanation takes place in position 1 with formation of compound **15**. However, its cyclization occurs even under mild reaction conditions, which leads to simultaneous production of naphthothiazole derivative **16**. Compounds **10** – **15**, display a characteristic sharp absorption band in the region of 2151-2156 cm<sup>-1</sup> in ir spectrum. With compounds **6** – **8** bearing a thiocyanato

Chart



group on the nitrogen atom this absorption band is shifted to longer wavelengths (2127-2136 cm<sup>-1</sup>).

The reaction of **3** with phenols (hydroquinone, 2-naphtol) were conducted under the same conditions as reactions with amines. As distinguished from amines, however, the reaction proceeded very slowly even under boiling producing complex reaction mixtures. A similar reaction course was

observed in the reaction of **3** with  $\alpha$ -dicarbonyl compounds (5,5-dimethyl-1,3-cyclohexanedione, ethyl 3-oxobutyrate) from which we failed to obtain pure products. In both cases we recorded formation of a yellow polymeric material, production of which during decomposition of  $\alpha$ -thiocyanato- $\alpha$ -ketoesters was described also by Prakash *et al.* [12].

The reaction of **3** with thiols affords disulfides (**17**, **18**, and **19**) (Chart). We suppose that cyano disulfanes **A** primarily arise, but they react under given reaction conditions with another molecule of thiol to form disulfides **17-19** (Scheme 3). High reactivity of compounds **A** towards nucleophiles is well-known [18]. According to Scheme 3, half the molar quantity of reagent **3** is sufficient. Indeed, under these reaction conditions (Method D), yields of disulfides **17-19** are comparable to or even higher than those attained when equimolar reactant mixtures (Method C) were used. A further increase in yield of disulfides comes about when the reaction is performed in presence of solid potassium carbonate that neutralized forming thiocyanic acid (Method E).

Reagent **3** evidently reacts the more readily, the more nucleophilic is its reaction partner. Ylides are strong nucleophiles, and we also proved the reaction of ethyl (triphenyl-

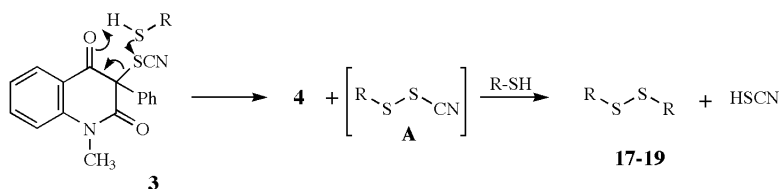
$\text{CDCl}_3$ ,  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are given on the scale (ppm) and are referenced to internal TMS. Mass spectra were obtained on a VG-Analytical AutospecQ instrument. Column chromatography was carried out on silica gel 70-230 mesh, 60 Å (Aldrich) using benzene and then successive mixtures of benzene – ethyl acetate (in ratios from 99:1 to 8:2). The course of separation and also the purity of substances were monitored by tlc (elution systems benzene-ethyl acetate, 4:1 and chloroform-ethanol, 9:1) on Alugram® SIL G/UV254 foils (Macherey-Nagel). Elemental analyses (C, H, N) were performed on EA 1108 Elemental Analyser (Fisons Instrument).

Starting 1-methyl-3-phenyl-3-thiocyanato-1*H*,3*H*-quinoline-2,4-dione (**3**), mp 169-171 °C, was prepared according to Ref. [1].

4-Hydroxy-1-methyl-3-phenyl-1*H*-quinolin-2-one (**4**).

a) A solution of **3** (616 mg, 2 mmoles) in methanol (10 ml) was refluxed for 1 hour. According to tlc, no reaction occurred. The solution was subsequently cooled and split into two same parts. Conc. HCl (2 drops) was added to the first part and the solution was left to stand for 5 h. It was subsequently evaporated to dryness *in vacuo* and residue was crystallized from ethanol. Compound **4** was obtained in 83% yield (210 mg), mp 223-225 °C (ethanol), according to ir spectra identical with authentic sample, mp 226 °C, prepared after Ref. [19]. Powdered sodium

Scheme 3



phosphoranylidene)acetate with **3** already proceeds at room temperature and compound **20** is formed in high yield.

Concluding, we would like to observe that to the best of our knowledge compound **3** is the first thiocyanation agent with which the thiocyanato group is transferred from carbon atom. Not only compound **3** but also other known [1] 3-thiocyanato-1*H*,3*H*-quinoline-2,4-diones (**2**) could become useful reagents for thiocyanation of aliphatic amines, anilines and ylides. The ready availability of compounds **2** as well as simple reaction protocol represent an advantage over thiocyanation methods employing thiocyanogen or thiocyanogen chloride. Employment of compounds **2** could also be advantageous for oxidizing thiols to disulfides.

## EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. The ir spectra were recorded on a Mattson 3000 spectrophotometer using samples in potassium bromide disks. The nmr spectra were recorded on a Bruker Avance spectrometer (500.13 MHz for  $^1\text{H}$  and 125.76 MHz for  $^{13}\text{C}$ ) in  $\text{DMSO}-d_6$  or

hydroxide (40 mg) was added to the second part of solution and that was stirred for 1 h. It was subsequently evaporated to dryness, residue was dissolved in water (5 ml) and acidified with conc. HCl. Deposited precipitate was filtered with suction and washed with water. After drying, compound **4** was obtained in 78% yield (198 mg), mp 223-224 °C.

b) Powdered zinc (196 mg, 3 mmoles) was added in small portions to a stirring solution of **3** (308 mg, 1 mmole) in acetic acid (5 ml) during 1 h at 50 °C. The reaction mixture was filtered and the filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in 0.5 *M* sodium hydroxide (5 ml), filtered and the filtrate was acidified with conc. HCl. The deposited precipitate was filtered with suction. After drying, compound **4** was obtained in 63% yield (159 mg), mp 222-224 °C.

4-Acetoxy-1-methyl-3-phenyl-1*H*-quinolin-2-one (**5**).

A solution of **3** (308 mg, 1 mmol) in acetic acid (5 ml) was refluxed for 1 hour. According to tlc, no reaction occurred. No reaction occurred even after acetic anhydride (0.5 ml) was added and the solution let to boil for an hour. After adding solid ammonium acetate (154 mg, 2 mmoles), the solution was boiled for another hour and then evaporated to dryness *in vacuo*. The residue was crystallized from ethanol and compound **5** was obtained in 75% yield (220 mg), mp 187-190 °C; for **5**, mp 184-187°C is reported [20].

General Procedures for the Reaction of **3** with Aliphatic Amines and Anilines.

#### Method A.

A solution of corresponding amine (2 mmoles) in benzene (20 ml) was added to a solution of **3** (616 mg, 2 mmoles) in benzene (50 ml). The mixture was stirred at room temperature for 1 h and subsequently refluxed for a time determined by tlc monitoring. After cooling, deposited compound **4** was filtered with suction, the reaction mixture was evaporated to half of its volume and a further portion of deposited compound **4** was filtered with suction. The filtrate was evaporated to dryness *in vacuo* and residue crystallized from appropriate solvent or column chromatographed.

#### Method B.

The reactions were carried out by the same manner as is described in Method A, but chloroform was used as solvent instead of benzene.

#### *N*-Benzyl-S-cyanothiohydroxylamine (**6**).

Compound **6** was prepared by the reaction of **3** with benzylamine using Method A (reflux 3.5 h), and was obtained after column chromatography as pale yellow oil in 73% yield (239 mg); ir: 3301, 3029, 2854, 2136, 1600, 1494, 1457, 1410, 1339, 1309, 1294, 1204, 1080, 1033, 1024, 870, 789, 746, 698, 613, 598  $\text{cm}^{-1}$ , identical with that of compound **6** prepared according to Ref. [16].

#### *N,N*-Dibenzyl-S-cyanothiohydroxylamine (**7**).

Compound **7** was prepared by the reaction of **3** with dibenzylamine using Method A (reflux 3.5 h), and was obtained in 57% yield (289 mg), mp 46-47 °C (hexane); ir: 3025, 2849, 2127, 1600, 1495, 1453, 1446, 1370, 1360, 1311, 1253, 1204, 1101, 1071, 1029, 979, 948, 911, 746, 698, 621, 607  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (DMSO- $d_6$ ): 4.07 (s, 4H, two PhCH<sub>2</sub>), 7.37 (s, 10H, two Ph);  $^{13}\text{C}$  nmr (DMSO- $d_6$ ): 61.55, 110.35, 127.97, 128.47, 128.55, 128.97, 129.65, 136.17; ms:  $m/z$  (%): 196 (M<sup>+</sup>-SCN, 29), 120 (21), 106 (75), 91 (100), 77 (11), 65 (23), 59 (15).

Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>S (254.35): C, 70.83; H, 5.55; N, 11.01. Found: C, 70.72; H, 5.75; N, 10.82.

#### *N*-(2-(3,4-Dimethoxyphenyl)ethyl)-S-cyanothiohydroxylamine (**8**).

Compound **8** was prepared by the reaction of **3** with 2-(3,4-dimethoxyphenyl)ethylamine using Method B (6 h at room temperature), and was obtained after column chromatography as colorless oil in 54% yield (257 mg); ir: 3273, 2964, 2940, 2837, 2133, 1607, 1592, 1516, 1462, 1437, 1419, 1351, 1326, 1264, 1233, 1157, 1141, 1069, 1026, 900, 860, 808, 763, 661  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (CDCl<sub>3</sub>): 2.85 (t,  $J = 6.7$  Hz, 2H, ArCH<sub>2</sub>), 3.02 (t,  $J = 5.6$  Hz, 1H, NH), 3.31 (dd,  $J = 6.7$  and 5.6 Hz, 2H, CH<sub>2</sub>N), 3.85 (s, 3H, OCH<sub>3</sub>), 3.87 (s, 3H, OCH<sub>3</sub>), 6.70 (d,  $J = 2.1$  Hz, 1H, H-2), 6.73 (dd,  $J = 7.9$  and 2.1 Hz, 1H, H-6), 6.80 (d,  $J = 7.9$  Hz, 1H, H-5);  $^{13}\text{C}$  nmr (CDCl<sub>3</sub>): 34.71 (Ar-C), 54.18 (C-N), 55.86 (OCH<sub>3</sub>), 55.89 (OCH<sub>3</sub>), 111.40 (C-5), 111.74 (C-2), 114.17 (SCN), 120.67 (C-6), 130.12 (C-1), 147.86 (C-4), 149.12 (C-3).

Anal. Calcd. for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S (238.31): C, 55.44; H, 5.92; N, 11.76. Found: C, 55.12; H, 5.78; N, 11.85.

#### 2-(3,4-Dimethoxyphenyl)ethylammonium Thiocyanate (**9**).

Compound **9** was prepared by the reaction of **3** with 2-(3,4-dimethoxyphenyl)ethylamine using Method B, and was obtained

after column chromatography besides compound **8** in 27% yield (128 mg) as colorless crystals (ethyl acetate), mp 161-163 °C; ir:

3152, 3131, 3061, 3019, 2965, 2834, 2707, 2630, 2574, 2079, 1623, 1612, 1519, 1462, 1434, 1362, 1268, 1239, 1158, 1143, 1125, 1028, 874, 800, 767, 692, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (DMSO- $d_6$ ): 2.83 (t,  $J = 7.8$  Hz, 2H, Ar-CH<sub>2</sub>), 3.07 (t,  $J = 7.8$  Hz, 2H, CH<sub>2</sub>N), 3.77 (s, 3H, OCH<sub>3</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 6.81 (dd,  $J = 7.9$  and 2.1 Hz, 1H, H-6), 6.91 (d,  $J = 2.1$  Hz, 1H, H-2), 6.94 (d,  $J = 7.9$  Hz, 1H, H-5), 7.74 (br s, 3H, NH<sub>3</sub><sup>+</sup>);  $^{13}\text{C}$  nmr (DMSO- $d_6$ ): 32.79 (Ar-C), 40.31 (C-N), 55.58 (OCH<sub>3</sub>), 55.67 (OCH<sub>3</sub>), 112.12 (C-5), 112.63 (C-2), 120.76 (C-6), 129.62 (C-1), 130.01 (SCN), 147.81 (C-4), 148.93 (C-3).

Anal. Calcd. for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S (240.32): C, 54.98; H, 6.71; N, 11.66. Found: C, 54.77; H, 6.98; N, 11.49.

#### *N*-Ethyl-4-thiocyanatoaniline (**10**).

Compound **10** was prepared by the reaction of **3** with *N*-ethyl-aniline using Method A (reflux 4.5 h), and was obtained in 47% yield (166 mg), mp 53-54 °C (hexane); for **10**, mp 54 °C is reported [21]; ir: 3380, 2971, 2873, 2152, 1596, 1512, 1476, 1451, 1406, 1384, 1334, 1296, 1264, 1177, 1150, 1085, 815, 677  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (DMSO- $d_6$ ): 1.15 (t,  $J = 7.1$  Hz, 3H, CH<sub>3</sub>), 3.05 (m, 2H, NHCH<sub>2</sub>), 6.27 (t,  $J = 4.8$  Hz, 1H, NH), 6.63 (d,  $J = 8.7$  Hz, 2H, H-2 and H-6), 7.37 (d,  $J = 8.7$  Hz, 2H, H-3 and H-5);  $^{13}\text{C}$  nmr (DMSO- $d_6$ ): 13.99, 36.88, 104.42, 112.96, 113.07, 134.79, 150.91; ms:  $m/z$  (%): 178 (M<sup>+</sup>, 42), 163 (100), 152 (12), 134 (13), 118 (6), 105 (18), 97 (11), 85 (6), 81 (22), 77 (7), 69 (42), 63 (8), 57 (20).

Anal. Calcd. for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>S (178.26): C, 60.64; H, 5.65; N, 15.72. Found: C, 60.81; H, 5.47; N, 15.49.

#### *N*-Benzyl-4-thiocyanatoaniline (**11**).

Compound **11** was prepared by the reaction of **3** with *N*-benzyl-aniline using Method A (reflux 4.5 h) in 59% (283 mg), mp 41-2 °C (cyclohexane); for **11**, mp 78 °C (ethanol) is reported [22]. Compound **11** prepared by us according to Ref. [22] exhibits mp 40-41 °C (cyclohexane); ir: 3362, 3033, 2890, 2858, 2152, 1598, 1511, 1468, 1453, 1406, 1331, 1297, 1257, 1179, 1121, 1092, 820, 742, 696, 673, 531  $\text{cm}^{-1}$ .

Anal. Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>S (240.32): C, 69.97; H, 5.03; N, 11.66. Found: C, 69.71; H, 5.23; N, 11.42.

#### 2,5-Dimethyl-4-thiocyanatoaniline (**12**).

Compound **12** was prepared by the reaction of **3** with 2,5-dimethylaniline using Method B (reflux 1.5 h), and was obtained after column chromatography as the main reaction product in 65% yield (232 mg); colorless crystals, mp 59-61 °C (ethyl acetate); for **12**, mp 64 °C is reported [23]; ir: 3467, 3428, 3349, 3213, 2920, 2863, 2151, 1630, 1558, 1498, 1461, 1401, 1376, 1306, 1298, 1264, 1036, 893, 856, 799, 716, 673, 639, 582  $\text{cm}^{-1}$ .

#### 2-Amino-4,7-dimethyl-6-thiocyanatobenzothiazole (**13**).

Compound **13** was prepared by the reaction of **3** with 2,5-dimethylaniline using Method B (reflux 1.5 h), and was obtained after column chromatography besides compound **12** in 18% yield (85 mg); yellowish crystals, mp 240-241 °C; for **13**, mp 231 °C is reported [24]; ir: 3400, 3309, 3082, 2951, 2923, 2764, 2153, 1657, 1581, 1530, 1465, 1455, 1374, 1296, 1118, 1062, 1118, 1062, 852, 744, 710, 598  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (DMSO- $d_6$ ): 2.40 (s, 3H, Ar-CH<sub>3</sub>), 2.51 (s, 3H, Ar-CH<sub>3</sub>), 7.39 (s, 1H, Ar-H), 7.86 (s,

2H, NH<sub>2</sub>); <sup>13</sup>C nmr (DMSO-*d*<sub>6</sub>): 17.54, 20.13, 112.10, 126.41, 130.62, 132.32, 132.64, 153.65, 167.55; ms: *m/z* (%): 235 (M<sup>+</sup>, 100), 220 (6), 208 (18), 202 (49), 177 (14), 165 (8), 121 (6), 91 (6), 82 (6), 69 (7).

#### 3-Nitro-4-thiocyanatoaniline (**14**).

Compound **14** was prepared by the reaction of **3** with 3-nitroaniline using Method B (reflux 40 h), and was obtained in 8% yield (32 mg); orange crystals (ethanol), mp 152-153 °C; ir: 3485, 3449, 3380, 3364, 3084, 2156, 1621, 1561, 1503, 1476, 1314, 1301, 1241, 1167, 1114, 860, 830, 813, 755, 686, 650 cm<sup>-1</sup>; <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>): 6.32 (s, 2H, NH<sub>2</sub>), 7.14 (dd, *J*=7.3 and 2.0 Hz, 1H, H-6), 7.55 (d, *J*=2.0 Hz, 1H, H-2), 7.60 (d, *J*=7.3 Hz, 1H, H-5); <sup>13</sup>C nmr (DMSO-*d*<sub>6</sub>): 104.84, 109.74, 111.81, 120.95, 130.79, 146.68, 150.67.

*Anal.* Calcd. for C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>S (195.20): C, 43.07; H, 2.58; N, 21.53. Found: C, 43.23; H, 2.87; N, 21.28.

#### 1-Thiocyanato-2-naphthylamine (**15**).

Compound **15** was prepared by the reaction of **3** with 2-naphthylamine using Method A (reflux 3 h), and was obtained after column chromatography in 27% yield (109 mg), mp 152-154 °C (benzene); for **15**, mp 151-154 °C is referred [25].

#### 2-Aminonaphtho[2,1-*d*]thiazole (**16**).

Compound **16** was prepared by the reaction of **3** with 2-naphthylamine using Method A (reflux 3 h), and was obtained after column chromatography besides compound **15** in 33% yield (131 mg), mp 262-264 °C (benzene); for **16**, mp 264-6 °C is referred [25].

#### General Procedures for the Reaction of **3** with Thiols.

##### Method C.

A solution of corresponding thiol (1 mmol) in chloroform (20 ml) was added to a solution of **3** (308 mg, 1 mmole) in chloroform (30 ml). The reaction mixture was refluxed for 2 h. After cooling, the solution was twice extracted with 5-% solution of potassium carbonate. The organic layer was separated, dried and evaporated to dryness *in vacuo*. The residue was crystallized from appropriate solvent.

##### Method D.

The reactions were carried out by the same manner as is described in Method A, but 2 mmoles of corresponding thiol were used.

##### Method E.

A solution of corresponding thiol (2 mmoles) in chloroform (20 ml) was added to a solution of **3** (308 mg, 1 mmole) in chloroform (30 ml). After addition of 560 mg (4 mmoles) of powdered potassium carbonate, the reaction mixture was refluxed for 2 h, cooled and shaken with water (50 ml). The organic layer was separated, dried, and evaporated to dryness *in vacuo*. The residue was crystallized from appropriate solvent.

#### Diphenyl Disulfide (**17**).

Compound **17** was prepared by the reaction of **3** with thiophenol using Method C, and was obtained in 76% yield (83 mg), mp 57-59 °C (aqueous ethanol), identical in all respects with authentic specimen (Aldrich). Using Method D, compound **17**, mp 58-59 °C, was obtained in 85% yield (185 mg).

#### 2,2'-Dithiobis(benzothiazole) (**18**).

Compound **18** was prepared by the reaction of **3** with 2-sulfanylbenthiazole using Method C, and was obtained in 24% yield (40 mg), mp 177-178 °C, identical in all respects with authentic specimen (Aldrich). Using Method D, compound **18** was obtained in 30% yield (99 mg) and using Method E, compound **18** was obtained in 62% yield (207 mg).

#### Diacetyldisulfane (**19**).

Compound **19** was prepared by the reaction of **3** with thioacetic acid using Method D, and was obtained in 85% yield (128 mg), mp 20 °C, identical in all respects with authentic specimen prepared according to Ref. [26]. Using Method E, compound **19** was prepared in 88% yield (132 mg).

#### Ethyl (Triphenylphosphoranylidene)thiocyanatoacetate (**20**).

A solution of ethyl (triphenylphosphoranylidene)acetate (697 mg, 2 mmoles) in benzene (10 ml) was added to a solution of **3** (618 mg, 2 mmoles) in benzene (50 ml). The reaction mixture was stirred for 15 min at room temperature. Deposited crystals of **4** (452 mg, 90%) were filtered off and the filtrate was evaporated to dryness. Compound **20** was obtained in 85% yield (688 mg) by crystallization from methanol, mp 138-140 °C; for **20**, mp 139-142 °C is reported [27]. Performing the reaction in a solution of chloroform, compound **20** was obtained in 81% yield (663 mg), mp 140-141 °C (methanol).

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