2-Chloro-4,5-dihydroimidazole, Part X [1]. Revisiting route to *N*-heteroarylimidazolidin-2-ones

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The ureidation reactions of 2- and 4-picoline *N*-oxides with 2-chloro-4,5-dihydroimidazole are described. A mechanism of novel thioureidation reaction of 4-picoline *N*-oxide with 2-(4,5-dihydro-1*H*-imidazol-2-ylthioxy)-4,5-dihydro-1*H*-imidazole is proposed. Structural assignment is confirmed by ^{1}H and ^{13}C nmr as well as by X-ray crystallography.

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Introduction.

Recently, *N*-aryl and *N*-heteroarylimidazolidin-2-ones of type **A** (Figure 1) have emerged as important target molecules in organic synthesis because their derivatives can act as α_2-adrenoreceptor antagonists [2], dopamine D_2 receptor antagonists [3], antifungal [4] and antiviral agents [5]. Although a number of *N*-arylimidazolidin-2-ones have been prepared, only a few synthetic examples of *N*-heteroaryl counterparts have been reported [2,5-7].

Within the framework of the project directed towards the synthesis of novel imidazolidin-2-one derivatives acting at adrenergic and/or imidazoline receptors, we needed derivatives with picolin-2-yl moiety placed at the N^1-position. This prompted us to revisit the previously investigated route which utilizes reactions of 2-chloro-4,5-dihydroimidazole **1** with heteroaromatic *N*-oxides [7].

For many years the imidazoline derivative **1**, obtained by Trani [8] by chlorination of imidazolidine-2-thione, proved to be valuable building block for the synthesis of new heterocyclic compounds with various physiological properties [1,8,9]. Previously, we described reactions of **1** with quinoline or isoquinoline *N*-oxides leading to *N*-(2-heteroaryl)imidazolidin-2-ones **B** and 1.3-bis(heteroaryl)-imidazolin-2-ones **C** [7]. The crucial point in these reactions was "ureidation" of heteroaromatic *N*-oxides. We also found that pyridine *N*-oxide reacted with **1** to give unstable pyridinium salt **D** instead of the desired ureidation product (Figure 1).

In this article, we would like to report the first syntheses of imidazolidin-2-one derivatives bearing 2- and 4-picolin-2-yl moiety at the N^1 and N^2 position, as well as to discuss the unexpected formation of *N*-(4-picolin-2-yl)imidazolidin-2-thione.

Results and Discussion.

The reaction of 2-chloro-4,5-dihydroimidazole **1** with 2-picoline *N*-oxide carried out in methylene chloride proceeded exothermically and led to the formation of 1-(6-methylpyridin-2-yl)imidazolidin-2-one hydrochloride **2**,

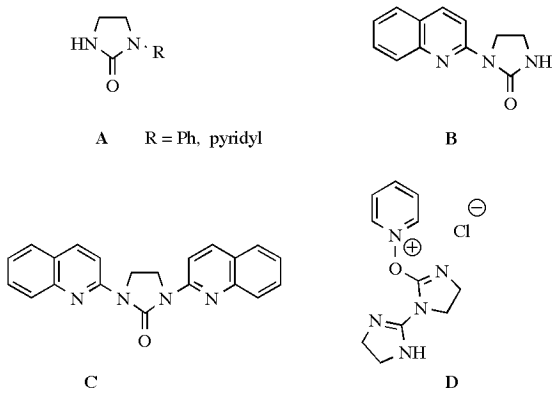


Figure 1

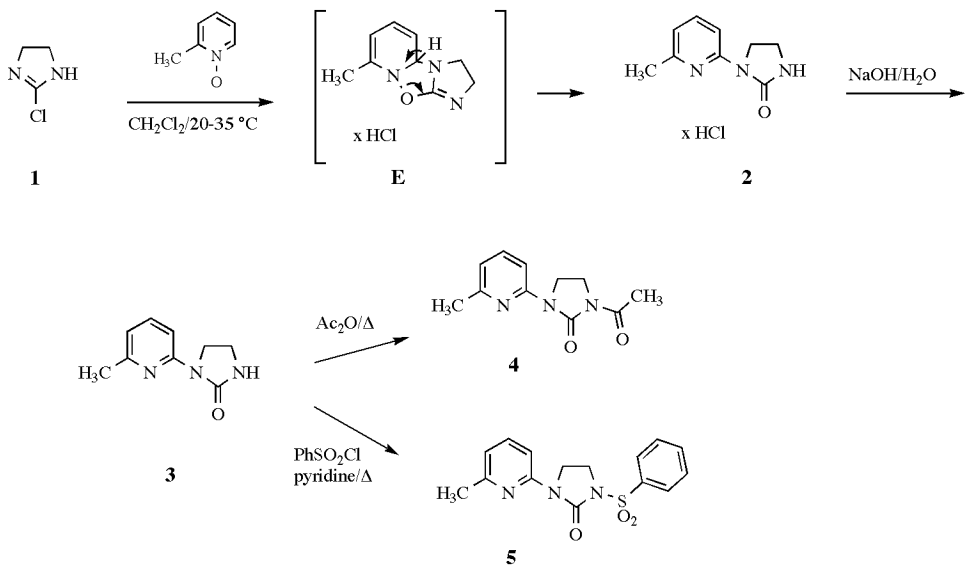
which upon treatment with aqueous sodium hydroxide afforded free base **3** in 26 % yield. Although the mechanism of the reaction leading to **2** was not studied in detail, we presume the initial step is the addition of compound **1** to the *N*-oxide with formation of intermediate **E**. Loss of hydrogen chloride molecule from **E** with simultaneous rearomatization gives rise to the product **2.** A similar mechanism has been proposed by Abramovitch *et al*., for the acylamination reaction of heteroaromatic *N*-oxides with imidoyl chlorides [10]. However, in our case, no side-chain ureidation product was found in the reaction mixture [11].

The ^{1}H nmr spectrum of the free base **3** exhibited characteristic pair of multiplets at 3.3-3.45 and 3.9-4.05 ppm (δ). In the ^{13}C nmr spectrum the cyclic ureido C=O signal at 158.64 ppm (δ) is also consistent with the proposed structure.

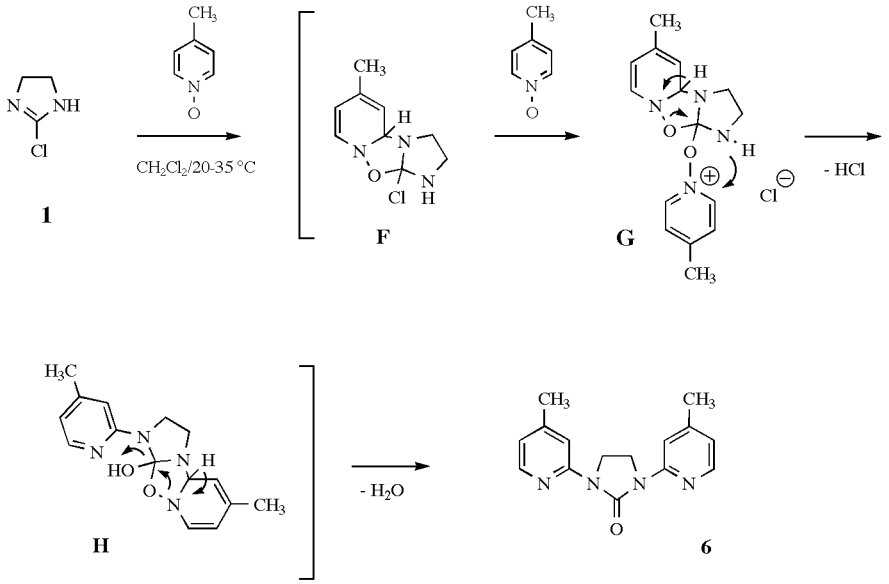
Further reactions of **3** with acetic anhydride or benzenesulfonyl chloride gave the amide **4** and sulfonamide **5**, respectively, as illustrated in Scheme 1.

On the other hand, the reaction of **1** with 4-picoline *N*-oxide afforded 1,3-bis(4-picolin-2-yl)imidazolidin-2-one **6** as a free base, according to the Scheme 2. The reaction involves formation of the unstable adduct **F**, which *in situ*

Scheme 1



Scheme 2



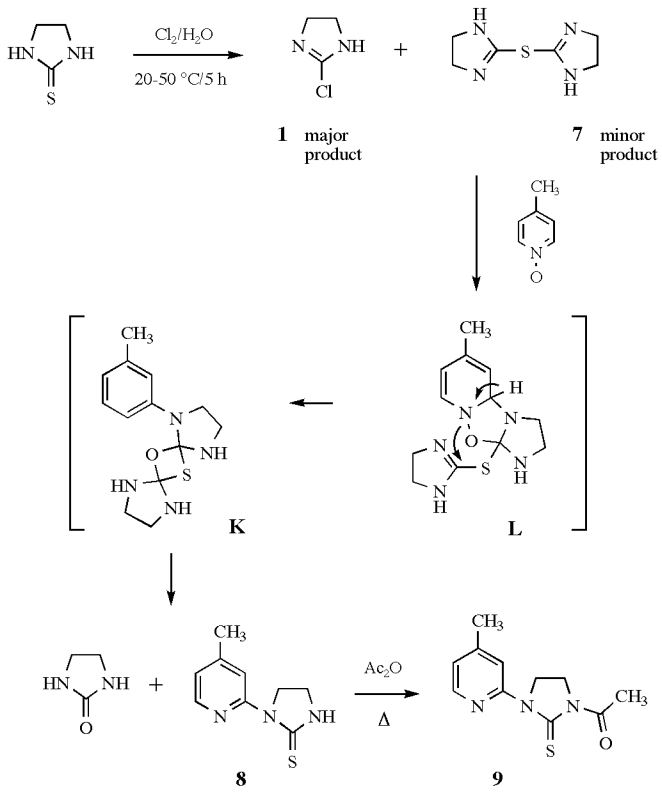
undergoes reaction with a second molecule of *N*-oxide to give **G**. The later intermediate undergoes further rearrangement with elimination of hydrogen chloride leading to **H** followed by loss of water to give the final product **6**. Although, concomitant formation of monosubstituted imidazolidin-2-one was possible, this product was not detected by means of ^{1}H nmr.

It has to be pointed out that compound **1** proves to be extremely unstable as a free base, and therefore, it has to be stored in form of either the hemisulfate or hydrochloride [8]. The results described above could be achieved only when pure starting material **1** was used for the reactions. However, when the compound **1** was liberated from crude (uncrystallized) hemisulfate, and subsequently subjected to the reaction with 4-picoline *N*-oxide, a mixture of two products was formed and we found that the 1,3-disubstituted imidazolidin-2-one **6** was accompanied by a sulfur-containing compound. The latter product was separated by preparative thick layer chromatography and characterized as 1-(4-methylpyridin-2-yl)imidazolidin-2-thione **8** (Scheme 3). This pathway proved to be only a side reaction giving **7** in no more than 7% yield.

From these results it was apparent that the chlorination reaction of imidazolidin-2-thione performed according to the original procedure [8] led to a mixture of products and the desired 2-chloro-4,5-dihydroimidazole **1** was accom-

panied by a sulfur-containing compound. From the reaction mixture we were able to separate 2-(4,5-dihydro-1*H*-imidazol-2-thioxo)-4,5-dihydro-1*H*-imidazole **7** (see experimental part) which we believe reacted with 4-picoline *N*-oxide to give **8** as described in Scheme 3.

Scheme 3



The ^{13}C nmr spectrum of **8** shows the characteristic signal at 180.08 ppm attributable to the carbon atom of the thiocarbonyl group. As reported in the literature [12] between the chemical shift of the carbon nuclei in C=O and C=S groups of analogous compounds a linear empirical relationship exists which can be used as an aid to assignment of chemical shifts:

$$\delta\,(C{=}S) = 1.50\,\delta\,(C{=}O) - 57.5$$

On the basis of chemical shift evaluation of the imidazolidin-2-one **2** (δ (C=O) = 158.64 ppm) the predicted chemical shift value for the C=S carbon atom of the imidazolidin-2-thione **8** would be 179.5 ppm, which is in good agreement with the value determined experimentally (180.08 ppm).

The structure of **8** was further confirmed by X-ray crystallographic study (*vide infra*).

Likewise compound **3**, the acetylation of **8** with acetic anhydride led to the corresponding amide derivative **9** (Scheme 3).

Molecular and Crystal Structure of **8** [13].

The molecule of **8** may exist in two forms, *Z* and *E*. In the studied crystal it adopts the *E* form and is slightly non-planar due to steric interactions between the pyridine hydrogen atom at C3 and the thione group S atom. The strain within the molecule is released by slight pyramidization of the imidazolidine N7 atom, leading to the 0.656(4) Å deviation of the S1 atom from the pyridine ring plane with the C11 atom residing virtually in the plane, and by increase in the values of the valence angles S1-C8-N7 [129.7(1)°], C8-N7-C2 [130.0(1)°] and N7-C2-C3 [123.9(2)°]. In effect, the intramolecular C3-H···S1 contact of 2.54(2) Å is only a little shorter than the sum of appropriate van der Waals radii (2.61 Å for non-spherical approximation [14,15]). The imidazolidine ring is only slightly puckered, with the largest endocyclic torsion angle equal to 9.7(3)°, and adopts the envelope form with C10 as a flap (Figure 2).

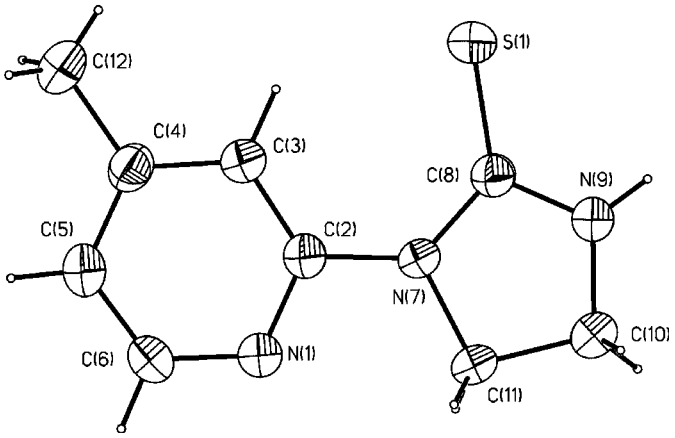


Figure 2. ORTEP drawing and atom labeling of **8**.

Bond lengths and angles within the imidazolidin-2-thione fragment of **7** compare well with those observed in the crystal structure of 1-thiocarbamoylimidazolidin-2-thione [16] with one exception. A weaker conjugation of the thioureido π-system with the pyridine ring is indicated by the bond lengths C2-N7 and N7-C8 of 1.406(2) and 1.376(2) Å, respectively, in the studied compound **8** and of 1.378 and 1.406 Å, respectively, in the thiocarbamoyl derivative. The C=S bond length of 1.670(3) Å, is close to the mean value of this bond for thioureas (1.681 Å [17]).

Conclusion.

We have shown that unlike pyridine *N*-oxide, 2- and 4-picoline *N*-oxides undergo ureidation upon treatment with 2-chloro-4,5-dihydroimidazole **1**. It was also found that chlorination of imidazolidin-2-thione furnishes 2-(4,5-dihydro-1*H*-imidazol-2-ylothioxy)-4,5-dihydro-1*H*-imidazole **7** as a side product, which could react with 4-picoline *N*-oxide to give thioureidation product **8**.

EXPERIMENTAL

All solvents were routinely dried and distilled prior to use. 2-Picoline *N*-oxide and 4-picoline *N*-oxide (Aldrich) were used as received. 2-Chloro-4,5-dihydroimidazole **1** was prepared and stored in the form of hemisulfate (mp 145-150 °C) or hydrochloride (mp 189-190 °C) according to the published procedure [8]. Nuclear magnetic resonance spectra were recorded on a Varian Gemini 200 apparatus. Infra red spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer. Mass spectra were recorded on a LKB 9000S spectrometer using EI method. Melting points were measured on a Buchi 535 apparatus and are uncorrected. Preparative thick layer chromatography was carried out using silica gel containing gypsum, Merck 60 PF_{254}. Column chromatography was carried out using Merck silica gel 60 (70-230 mesh ASTM).

1-(6-Methylpyridin-2-yl)imidazolidin-2-one (**3**).

To a stirred solution of 2-chloro-4,5-dihydroimidazole (**1**) (2.5 g, 24 mmol, obtained by treatment of the corresponding hydrochloride with cold 5% aqueous sodium hydroxide solution and extraction with methylene chloride) in methylene chloride (25 mL) was added 2-picoline *N*-oxide (2.18 g, 20 mmol). After the exothermic reaction had subsided (1 hour) the reaction mixture was allowed to stand at ambient temperature for 12 hours. Then, the solvent was evaporated under reduced pressure and the crude hydrochloride **2** was treated with 10% aqueous NaOH. The solid that precipitated (free base **3**) was separated by suction and after recrystallization from acetonitrile had mp 195-196 °C; yield 1.1 g (26 %); ir (KBr): 3218, 3113, 2895, 1704, 1590, 1464, 1399, 1346, 1263, 1146 cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.4 (s, 3H, CH_3), 3.3-3.45 (m, 2H, CH_2), 3.9-4.05 (m, 2H, CH_2), 6.8 (d, *J* = 7 Hz, 1H, CH), 7.16 (br s, 1H, NH), 7.5 (t, 1H, CH), 7.95 (d, *J* = 8.4 Hz, 1H, CH); ^{13}C nmr (DMSO-d_6): δ 24.36, 36.71, 43.72, 109.0, 116.4, 137.65, 152.32, 156.0, 158.64; ms: m/z 177 (M^+,100), 176 (53.5), 135 (8.6), 134 (18.8), 133 (63), 121 (23.7), 93 (57.9), 92 (32.9), 66 (13.3), 65 (24.6).

Anal. Calcd. for $C_9H_{11}N_3O$: C, 61.03; H, 6.26; N, 23.72. Found: C, 60.98; H, 6.15; N, 23.88.

1-Acetyl-3-(6-methylpyridin-2-yl)imidazolidin-2-one (**4**).

Compound **3** (0.47 g, 2.66 mmol) was dissolved in acetic anhydride (5 mL) and the solution thus obtained was refluxed for 6 hours. The reaction mixture was treated with water (15 mL) and made alkaline (pH 10) with aqueous solution of $NaHCO_3$. The aqueous solution was extracted with chloroform (3 x 15 mL). The organic phase was separated, dried with anhydrous Na_2SO_4 and evaporated to dryness. Crude product **4** thus obtained was triturated with ethyl ether, and then separated by filtration and purified by crystallization from methanol; mp 140-143 °C; yield 0.35 g, (60 %); ir (KBr): 2923, 1724, 1666, 1504, 1456, 1388 cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.45 (s, 3H, CH_3), 3.1 (s, 3H, CH_3), 3.7-3.85 (m, 2H, CH_2), 3.9-4.05 (m, 2H, CH_2), 6.95 (d, *J* = 7 Hz, 1H, CH), 7.65 (t, 1H, CH), 7.95 (d, *J* = 7 Hz, 1H, CH).

Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.97; N, 19.16. Found: C, 60.01; H, 6.12; N, 19.32.

1-Benzenesulfonyl-3-(6-methylpyridin-2-yl)imidazolidin-2-one (**5**).

To a solution of **3** (0.67 g, 3.79 mmol) in anhydrous pyridine (8 mL) was added dropwise benzenesulfonyl chloride (1.35 mL, 7.5 mmol), and the reaction mixture was heated under reflux for 6 hours. Then, the solution was cooled to room temperature and treated with water (15 mL). The crude product **5** thus obtained was separated by filtration and purified by crystallization from methanol; mp 174-175 °C; yield 0.61 g (51 %); ir (KBr): 2912, 1723, 1584, 1456, 1360, 1240, 1180 cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.4 (s, 3H, CH_3), 3.95-4.05 (m, 4H, CH_2), 6.95 (d, *J* = 7.5 Hz, 1H, CH), 7.45-7.82 (m, 6H, aromat.), 8.05 (d, *J* = 7.5 Hz, 1H, CH); ^{13}C nmr (DMSO-d_6): δ 24.2, 41.13, 41.7, 109.8, 118.7, 128.1, 129.7, 134.6, 137.7, 138.5, 150.2, 151.4, 156.6.

Anal. Calcd. for $C_{15}H_{15}N_3O_3S$: C, 56.76; H, 4.76; N, 13.24. Found: C, 56.51; H, 4.52; N, 13.46.

1,3-Bis(4-methylpyridin-2-yl)imidazolidin-2-one (**6**).

To a solution of **1** (2.5 g, 24 mmol, obtained by treatment of the corresponding hydrochloride with cold 5% aqueous sodium hydroxide solution and extraction with methylene chloride) in methylene chloride (25 mL) was added 4-picoline *N*-oxide (3.27 g, 30 mmol). The reaction mixture was stirred until the exothermic reaction had subsided (1 hour), and then, left overnight at room temperature. The solvent was evaporated under reduced pressure and the oily residue was treated with water (10 mL). Crude product **6** that precipitated was collected by filtration and purified by crystallization from methanol; mp 189-191 °C; yield 0.73 g (22 %); ir (KBr): 2967, 2910, 1721, 1605, 1560, 1482, 1460, 1413, 1392, 1305, 1241 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.39 (s, 6H, CH_3), 4.18 (s, 4H, CH_2), 6.83 (d, *J* = 4.5 Hz, 2H, CH), 8.19 (s, 2H, CH), 8.21 (d, *J* = 4.5 Hz, 2H, CH); ^{13}C nmr (deuteriochloroform): δ 20.72, 40.11, 113.04, 119.07, 146.4, 148.02, 151.57, 153.83; ms: m/z 268 (M^+, 38.6), 135 (94.1), 134 (100), 133 (90.2), 93 (22.5), 92 (30.9), 66 (11.4), 65 (24.7).

Anal. Calcd. for $C_{15}H_{16}N_4O$: C, 67.14; H, 6.01; N, 20.88. Found: C, 67.07; H, 5.91; N, 20.99.

1-(4-Methylpyridin-2-yl)imidazolidin-2-thione (**8**) and 1,3-Bis(4-methylpyridin-2-yl)imidazolidin-2-one (**6**).

Reaction of Crude **1** with 4-Picoline *N*-Oxide.

To a solution of crude **1** (obtained by treatment of the corresponding hemisulfate, 5 g, 25 mmol, with cold 5% aqueous sodium hydroxide solution and extraction with methylene chloride) in methylene chloride (25 mL) was added 4-picoline *N*-oxide (2.7 g, 25 mmol). The reaction mixture was stirred until the exothermic reaction had subsided (1 hour), and then, left overnight at room temperature. The solvent was evaporated under reduced pressure and the oily residue was treated with water (10 mL) and extracted with chloroform (3 x 10 mL). The combined organic layers were dried with anhydrous sodium sulfate and evaporated to dryness. After separation by preparative thick layer chromatography (chloroform/methanol 16:1) the following products were obtained: compound **6** (R_f = 0.9, 17 % yield) and compound **8** (R_f = 0.78) as colorless needles (acetonitrile), mp 202-204 °C, 7% yield; ir (KBr): 3260, 3066, 2895, 1610, 1517, 1476, 1406, 1233 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.7 (t, 2H, CH_2), 4.45 (t, 2H, CH_2), 6.63 (br s, 1H, NH), 6.9 (d, *J* = 5.5 Hz, 1H, CH), 8.24 (d, *J* = 5.5 Hz, 1H, CH), 8.76 (s, 1H, CH); ^{13}C nmr (DMSO-d_6): δ 21.14, 40.65, 49.18, 116.49, 120.6, 147.26, 152.90, 180.08; ms: m/z 193 (M^+, 100), 192 (44.5), 134, (37.2), 133 (82.4), 121 (75), 93 (19.6), 92 (48.9).

Anal. Calcd. for $C_9H_{11}N_3S$: C, 55.92; H, 5.74; N, 21.74. Found: C, 56.12; H, 5.56, N, 21.49.

1-Acetyl-3-(4-methylpyridin-2-yl)imidazolidin-2-thione (**9**).

Compound **9** was obtained according to the acetylation procedure described above for **4** and after crystallization from methanol had mp 105-107 °C; yield 69 %; ir (KBr): 3013, 2966, 1677, 1596, 1476, 1466, 1399, 1364, 1307, 1261, 1254, 1246 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.44 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 4.08-4.2 (m, 2H, CH_2), 4.22-4.33 (m, 2H, CH_2), 7.03 (d, *J* = 5 Hz, 1H, CH), 8.23 (s, 1H, CH), 8.33 (d, *J* = 5 Hz, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 21.77, 27.69, 44.25, 46.67, 120.79, 123.3, 148.28, 148.89, 152.2, 172.54, 178.3; ms: m/z 235 (M^+, 64.6), 192 (28.4), 134 (18.6), 133 (39.8), 121 (100), 120 (12.2), 92 (22.9).

Anal. Calcd. for $C_{11}H_{13}N_3OS$: C, 56.15; H, 5.57; N, 17.86. Found: C, 56.01; H, 5.33; N, 17.89.

Separation of 2-(4,5-Dihydro-1*H*-imidazol-2-ylthioxy)-4,5-dihydro-1*H*-imidazole (**7**).

To a solution of crude **1** (obtained by treatment of the corresponding hemisulfate, 5 g, 25 mmol, with cold 5% aqueous sodium hydroxide solution and extraction with methylene chloride) in methylene chloride (25 mL) was added pyridine (3 mL) and the reaction mixture was stirred until the exothermic reaction had subsided (1 hour). Then, diethyl ether was added (10 mL) and the solid that precipitated (product of cyclocondensation reaction of **1** and pyridine in form of hydrochloride (see ref. [18]) was separated by suction. The filtrate was evaporated to dryness under reduced pressure and the oily residue was purified by column chromatography (chloroform/diethyl ether, 5:1). Pure compound **7** thus obtained (20 mg) proved to be thermally unstable and melted with decomposition at 150-156 °C; ir (KBr): 3265, 2887, 1519, 1498, 1464, 1310, 1276, 1205 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.62 (s, 8H, CH_2), 8.98 (br. s, 2H, NH).

Anal. Calcd. for $C_6H_{10}N_4S$: C, 42.33; H, 5.92; N, 32.9. Found: C, 41.91, H, 5.76; N, 32.61.

X-Ray Structure Analysis of Compound (**8**).

Crystal data for $C_9H_{11}N_3S$: monoclinic, space group $P2_1/c$, a = 10.6787(9), b =11.8828(8), c = 7.5122(7) Å, β = 104.924(8)°, V = 921.1(1) $Å^3$, Z = 4, d_x = 1.394 $g.cm^{-3}$, T = 293K. Data were collected for a crystal with dimensions 0.6x0.2x0.07 mm on a KumaCCD diffractometer using graphite monochromated Mo K_α radiation with detector-to-crystal distance of 6 cm. More than hemisphere of the reciprocal space was covered by combination of four sets of exposures; each set had a different ϕ-angle (0, 90, 180, 270) and each exposure of 30s covered 0.75° in ω. Out of 5102 reflections measured up to $2\theta_{max}$ = 26.37° 1867 were independent and used in further calculations. The structure was solved by direct methods with the program SHELXS-97 [19] and refined by full-matrix least-squares on F^2 with SHELXL-97 [20]. Hydrogen atoms have been located on ΔF map and their parameters included in the refinement process. Final R indices for 1602 reflections with $I>2\sigma(I)$ and 162 refined parameters are: R_1=0.0433, wR_2=0.1093 (R_1=0.0521, wR_2=0.1153for all data).

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[13] Crystallographic data for the structure of **8** have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC 183581. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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