# Chemistry of Sulfonyl Isocyanates and Sulfonyl Isothiocyanates. X. Possible Routes to Substituted Imidazolidinethiones and Hexahydropyrimidinethiones



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Received July 16, 1979

4-Toluenesulfonyl isocyanate (I) reacted with 2-aminoethanol and 3-amino-1-propanol to give 2:1 isocyanate/amino alcohol addition products. 1-Amino-2-propanol and I gave 1:1 and 2:1 adducts while 2-amino-2-methyl-1-propanol afforded only a 1:1 adduct. 4-Toluenesulfonyl isothiocyanate (III) gave 1:1 adducts with 2-aminoethanol, 1-amino-2-propanol and 3-amino-1-propanol, the first two of which were cyclized by concentrated sulfuric acid to 1-(4-toluenesulfonyl)-imidazoline-2-thiones and the third to 1-(4-toluenesulfonyl)hexahydropyrimidine-2-thione. A 1:2 adduct was obtained from III and 2-amino-2-methyl-1-propanol. Amino acids reacted with I and with 4-chlorobenzenesulfonyl isocyanate (II) to give *N*-(arylsulfonyl)-*N*$^1$-(carboxylic acid)-ureas. *N*-(4-Toluenesulfonyl)-*N*$^1$-(acetic acid)-urea (XVI) was converted to the methyl ester (XIX) by concentrated sulfuric acid and methanol and to water-soluble unrecoverable products by sulfuric acid alone. Glycine and III gave *N*-(4-toluenesulfonyl)-*N*$^1$-(acetic acid)-thiourea (XX) which was converted to the methyl ester (XXII) by concentrated sulfuric acid/methanol and to the cyclic 1-(4-toluenesulfonyl)imidazolin-5-one-2-thione (XXI) by sulfuric acid alone.

*J. Heterocyclic Chem.*, **17**, 273 (1980).

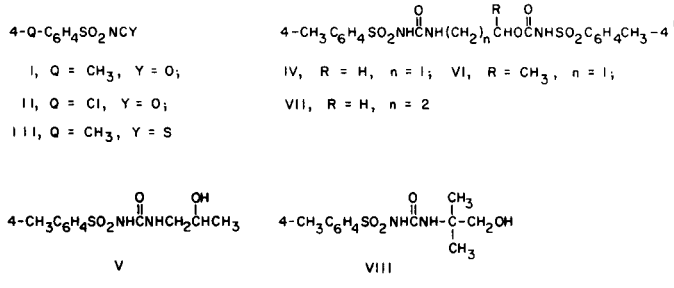
The reactions of amines and alcohols with either sulfonyl isocyanates or sulfonyl isothiocyanates have been extensively studied (5-18). Very little attention has been given to amino alcohols in which both functional groups may possibly react with either isocyanate or isothiocyanate (19). Sulfonyl isocyanates have been shown to react with carboxylate salts to afford *N*-acylsulfonamides (20), and with amino acids to give *N*-tosylaminocarbonyl derivatives (21). Benzenesulfonyl isothiocyanate and glycine produced a thiourea which cyclized upon treatment with concentrated sulfuric acid in methanol (6).

In this paper we show the results of the reaction of sulfonyl isocyanates and isothiocyanates with bifunctional amino alcohols and amino acids. Four amino alcohols were allowed to react with 4-toluenesulfonyl isocyanate (I). 2-Aminoethanol and 3-amino-1-propanol gave 2:1 isocyanate/amino alcohol adducts (IV and VII, respectively) when 1:1 ratios of reagents were used. Under similar conditions 1-amino-2-propanol gave both 1:1 and 2:1 adducts (V and VI), while 2-amine-2-methyl-1-propanol afforded the 1:1 addition product (VIII). Attempts at cyclizing V using concentrated sulfuric acid in methanol gave largely starting material.

4-Toluensulfonyl isothiocyanate (III) showed greater discrimination between the amino and hydroxyl groups. 2-Aminoethanol, 1-amino-2-propanol, and 3-amino-1-propanol all reacted with III to give 1:1 adducts (IX, XI, and XIII, respectively). That the amino group rather than the hydroxyl group had reacted was evidenced by ir and nmr spectroscopy and by the fact that IX, XI, and XIII were cyclized to X, XII, and XIV, respectively, by concentrated sulfuric acid in methanol. One of the cyclic thioureas, X, was studied and found to be stable toward refluxing 10% sodium hydroxide and 6*M* hydrochloric acid solutions. 2-Amino-2-methyl-1-propanol and III gave compound XV, consisting of one mole of isothiocyanate and two moles of amino alcohol. Product XV dissolved in a solution of concentrated sulfuric acid in methanol but quantitatively precipitated upon dilution with water.

Glycine reacted in boiling carbon tetrachloride with I and with 4-chlorobenzenesulfonyl isocyanate (II) to give *N*-(arylsulfonyl)-*N*$^1$-(acetic acid)-ureas (XVI and XVII, respectively). Alanine and phenylalanine also reacted with I to afford difficultly purified products (XVIII from phenylalanine). Attempts at cyclizing XVI were unsuccessful. Concentrated sulfuric acid and methanol produced the methyl ester XIX, while concentrated sulfuric acid alone gave unrecoverable products.

Glycine and III afforded *N*-(4-toluenesulfonyl)-*N*$^1$-(acetic acid)-thiourea (XX) which was converted to the methyl ester XXII by concentrated sulfuric acid and methanol, and to 1-(4-toluenesulfonyl)imidazolidin-5-one-2-thione (XXI) by acid alone.

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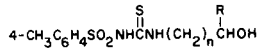
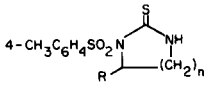


IX, R = H, n = 1;

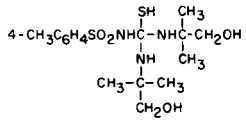
XI, R = $CH_3$, n = 1;

XIII, R = H, n = 2

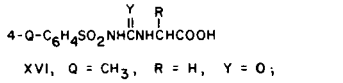


X, R = H, n = 1; XII, R = $CH_3$, n = 1;

XIV, R = H, n = 2



XV

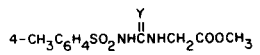


XVI, Q = $CH_3$, R = H, Y = O;

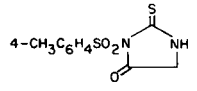
XVII, Q = Cl, R = H, Y = O;

XVIII, Q = $CH_3$, R = $CH_2C_6H_5$, Y = O;

XX, Q = $CH_3$, R = H, Y = S



XIX, Y = O; XXII, Y = S



XXI

## EXPERIMENTAL

4-Toluenesulfonyl isocyanate (I) and 4-chlorobenzenesulfonyl isocyanate (II) were purchased, respectively, from the Aldrich Chemical Company and the Upjohn Co., Carwin Organic Chemicals, and used without further purification. 4-Toluenesulfonyl isothiocyanate (III) was prepared by the methods of McFarland and Houser (6) and of Dickore and Kuehle (22). The ir spectra were recorded on a Perkin-Elmer 137 Spectrophotometer, using potassium bromide pellets, and the nmr spectra on a Hitachi HR-20 Nuclear Magnetic Resonance Spectrometer. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were by Midwest Microlab, Inc., Indianapolis, Indiana.

2-(*N*-4-Toluenesulfonyl-*N*$^1$-ureido)ethyl 4-Toluenesulfonyl Carbamate (IV).

A solution of 15.85 g. (0.08 mole) of 4-toluenesulfonyl isocyanate (I) in 50 ml. of dry ether was added dropwise with stirring under nitrogen to a solution of 4.92 g. (0.081 mole) of 2-aminoethanol in 50 ml. of dry ether during 15 minutes. The mixture was stirred an additional 1 hour at RT. The resulting white precipitate amounted to 16.49 g. (90.6%), m.p. 168-171°. Washing with cold water followed by drying gave IV with m.p. 169-171°; ir: 3250, 3100, 3050, 2900, 1700, 1650, 1550, 1340, ($SO_2$), 1150 ($SO_2$) $cm^{-1}$; nmr (perdeuterioacetone): δ 2.4 (6H singlet, $2CH_3$), δ 3.3 (2H multiplet, -NH-C$H_2$-$CH_2$-), δ 4.0 (2H triplet, -$CH_2$-C$H_2$O-), δ 7.3 (4H doublet, aromatic), δ 7.85 (4H doublet, aromatic).

*Anal.* Calcd. for $C_{16}H_{21}N_3O_7S_2$: C, 47.47; H, 4.62; N, 9.23. Found: C, 47.30; H, 4.75; N, 9.19.

*N*-(4-Toluenesulfonyl)-*N*$^1$-[1-(2-hydroxypropyl)]urea (V) and 1-(*N*-4-Toluenesulfonyl-*N*$^1$-ureido)-2-propyl 4-Toluenesulfonyl Carbamate (VI).

A solution of 8.93 g. (0.045 mole) of I and 3.42 g. (0.046 mole) of 1-amino-2-propanol in 100 ml. of chloroform was heated under reflux while stirring in a nitrogen atmosphere for 6 hours. After the solution stood for 4 days a white solid had precipitated which amounted to 2.38 g. (19.4%) of V, m.p. 137-139°; ir: 3425 (O-H), 3300 (N-H), 3050, 2875, 1660, 1575, 1335, 1160, $cm^{-1}$; nmr (perdeuterioacetone): δ 1.0 (3H doublet), δ 2.3 (3H singlet), δ 3.1 (2H multiplet, -$CH_2$-), δ 3.7-4.1 (∿3H; -CH-, -OH, -NH), δ 7.3 (2H doublet), δ 7.8 (2H doublet).

*Anal.* Calcd. for $C_{11}H_{16}N_2O_4S$: C, 48.53; H, 5.88; N, 10.29. Found: C, 48.48; H, 6.14; N, 10.16.

To the above chloroform filtrate was added petroleum ether to cloudiness at the boiling point. Upon cooling a waxy solid precipitated which was triturated with three 10-ml. portions of ether to afford 1.9 g., (18%) of white crystalline VI, m.p. 135-138°; m.m.p. with V, 120-133°; nmr (deuteriochloroform): δ 1.05 (3H doublet, -$CH_3$), δ 2.3 (6H singlet), δ 3.25 (2H broad, -$CH_2$-), δ 4.7 (1H broad, -CH-), δ 6.4 (1H broad, -CNHC$H_2$-?), δ 7.15 (4H doublet), δ 7.7 (4H doublet), δ 8.95 (∿2H broad, -$SO_2$NH-C-).

*Anal.* Calcd. for $C_{19}H_{23}N_3O_7S_2$: C, 48.61; H, 4.90; N, 8.95. Found: C, 48.79; H, 5.09; N, 8.71.

3-(*N*-4-Toluenesulfonyl-*N*$^1$-uriedo)-1-propyl 4-Toluenesulfonyl Carbamate (VII).

A solution of 8.18 g. (0.042 mole) of I and 3.2 g. (0.043 mole) of 3-amino-1-propanol in 100 ml. of chloroform was heated under reflux for 6 hours. The solvent was removed under reduced pressure to give 11.36 g. of gummy while solid. Recrystallization from acetone afforded 8.59 g. (87.2%) of VII, m.p. 162-166°. Subsequent recrystallization from chloroform:carbon tetrachloride gave pure VII, m.p. 168-169°; ir: 3300 (N-H), 3150 (N-H), 3000, 2900, 1675, 1550, 1340, 1155 $cm^{-1}$; nmr (perdeuterioacetone): δ 1.8 (2H quintuplet, -$CH_2$-C$H_2$$CH_2$-), δ 2.4 (6H singlet), δ 3.1 (2H multiplet, -NH-C$H_2$$CH_2$-), δ 3.9 (2H triplet, -$CH_2$-C$H_2$O), δ 7.3 (4H doublet), δ 7.8 (4H doublet). (Strong absorption at δ 2.1 indicated most of N*H* had exchanged with perdeuterioacetone).

*Anal.* Calcd. for $C_{19}H_{23}N_3O_7S_2$: C, 48.61; H, 4.90; N, 8.95. Found: C, 48.48; H, 5.31; N, 8.90.

*N*-(4-Toluenesulfonyl)-*N*$^1$-[2-(2-methyl-1-hydroxypropyl)]urea (VIII).

A solution of 10.77 g. (0.055 mole) of I in 50 ml. of dry ether was added to a solution of 4.89 g. (0.055 mole) of 2-amino-2-methyl-1-propanol in 25 ml. of dry ether during 15 minutes. The mixture was stirred an additional 1.5 hours at RT under nitrogen and the resultant white precipitate collected by suction filtration, weight 13.38 g. (85%), m.p. 114-118°. Recrystallization from chloroform produced VIII with m.p. 120-122°; ir: 3390 (-OH), 3250, 3100, 3050, 2900, 1675, 1600, 1340, 1160 $cm^{-1}$; nmr (deuteriochloroform): δ 1.2 (6H doublet), δ 2.3 (3H singlet), δ 2.6 (1H broad, OH?), δ 3.6 (2H doublet, -$CH_2$-), δ 3.85 (1H broad, -NH-?), δ 7.15 (2H doublet), δ 7.75 (2H doublet), δ 8.8 (∿1H, N-H?).

*Anal.* Calcd. for $C_{12}H_{18}N_2O_4S$: C, 50.35; H, 6.29; N, 9.79. Found: C, 50.10; H, 6.43; N, 9.71.

*N*-(4-Toluenesulfonyl)-*N*$^1$-(1-(2-hydroxyethyl))thiourea (IX).

A solution of 9.58 g. (0.045 mole) of 4-toluenesulfonyl isothiocyanate (III) in 15 ml. of dry chloroform was added during 30 minutes with stirring to a solution of 3.02 g. (0.045 mole) of 2-aminoethanol in 15 ml. of dry chloroform. After an additional 1.5 hours of stirring at ambient temperature, the precipitated white solid was collected by suction filtration and amounted to 9.35 g. (75.8%), m.p. 96-138°. Recrystallization from methanol:water gave IX with m.p. 140-142°; ir: 3350 (OH), 3230 (NH), 3000, 2900, 1600, 1390 (C=S), 1340 ($SO_2$), 1290 (C=S), 1145 ($SO_2$) $cm^{-1}$; nmr (perdeuterioacetone): δ 2.3 (3H singlet), δ 3.6 (4H multiplet), δ 7.3 (2H doublet), δ 7.8 (2H doublet), δ 8.6 (1H broad, -$SO_2$N*H*C-).

*Anal.* Calcd. for $C_{10}H_{14}N_2O_3S_2$: C, 43.80; H, 5.11; N, 10.22. Found: C, 43.73; H, 5.11; N, 10.38.

1-(4-Toluenesulfonyl)imidazolidine-2-thione (X).

To a cold solution of 2.5 g. (0.0091 mole) of IX in 20 ml. of methanol was added with stirring, 10 ml. of cold concentrated sulfuric acid. After standing at RT for 2 hours, the solution was poured into 30 ml. of ice water. The resulting white precipitate was collected by suction filtration, triturated with acetone, and dried to give 1.22 g. (52.1%) of X, m.p. 226-227°; ir: 3100, 3000, 2950, 1595, 1395, 1360, 1280, 1145 $cm^{-1}$.

*Anal.* Calcd. for $C_{10}H_{12}N_2O_2S_2$: C, 46.88; H, 4.69; N, 10.94. Found: C, 47.02; H, 4.80; N, 10.60.

*N*-(4-Toluenesulfonyl)-*N*$^1$-(1-(2-hydroxypropyl))thiourea (XI).

Using a procedure similar to that for preparing IX, except the mixture was heated 2 hours at 60-65°, 8.52 g. (0.04 mole) of III and 3.00 g. (0.04 mole) of 1-amino-2-propanol afforded 11.03 g. (95.7%) of XI, m.p. 96-115°. Recrystallization from chloroform gave product with m.p. 120-121.5°; ir: 3500, 3260, 3000, 2900, 1600, 1480, 1390, 1350, 1290, 1140 cm$^{-1}$.

*Anal.* Calcd. for $C_{11}H_{16}N_2O_3S_2$: C, 45.83; H, 5.55; N, 9.72. Found: C, 45.55; H, 5.72; N, 9.86.

1-(4-Toluenesulfonyl)-5-methylimidazolidine-2-thione (XII).

A solution of 1.5 g. (0.0052 mole) of XI, 20 ml. of methanol, and 7 ml. of concentrated sulfuric acid was heated at 50-60° for 2 hours, cooled, and poured into 30 ml. of ice water. The white precipitate (1.05 g., 75%) was collected by suction filtration, washed with water, and dried, m.p. 156-161°. Recrystallization from methanol:water gave XII with m.p. 164-166°; ir: 3100, 3000, 2900, 1600, 1395, 1340, 1295, 1140 cm$^{-1}$.

*Anal.* Calcd. for $C_{11}H_{14}N_2O_3S_2$: C, 48.89; H, 5.19; N, 10.37. Found: C, 48.60; H, 5.16; N, 10.38.

*N*-(4-Toluenesulfonyl)-*N*$^1$-(1-(3-hydroxypropyl))thiourea (XIII).

The procedure was identical to that used in synthesizing IX. From 8.52 g. (0.04 mole) of III and 3.00 g. (0.04 mole) of 3-amino-1-propanol was obtained 7.43 g. (64.5%) of XIII, m.p. 110-114°. Recrystallization from chloroform gave m.p. 114-116°; ir: 3400, 3150, 3000, 2900, 1390, 1340, 1290, 1140, cm$^{-1}$; nmr (perdeuterioacetone): $\delta$ 1.8 (2H quintuplet, -$CH_2CH_2CH_2$-), $\delta$ 2.4 (3H singlet), $\delta$ 3.6 (4H triplet, -N-$CH_2CH_2CH_2O$-), $\delta$ 7.35 (2H doublet), $\delta$ 7.85 (2H doublet), $\delta$ 8.65 (~1H broad, -$SO_2NHC$(=S)-). (Absorption at $\delta$ 2.05 indicative of exchange with perdeuterioacetone.)

*Anal.* Calcd. for $C_{11}H_{16}N_2O_3S_2$: C, 45.83; H, 5.56; N, 9.72. Found: C, 45.61; H, 5.56; N, 9.59.

1-(4-Toluenesulfonyl)hexahydropyrimidine-2-thione (XIV).

To a solution of 2.5 g. (0.0087 mole) of XIII in 20 ml. of methanol was added with stirring 10 ml. of cold concentrated sulfuric acid. After standing at RT for 2 hours the solution was poured into 30 ml. of cold water. The white precipitate weighed 1.63 g. (69.4%), m.p. 184-190°. Trituration with acetone gave pure XIV, m.p. 191-193.5°; ir: 3150, 3000, 2900, 1600, 1380, 1350, 1280, 1150 cm$^{-1}$.

*Anal.* Calcd. for $C_{11}H_{14}N_2O_3S_2$: C, 48.89; H, 5.19; N, 10.37. Found: C, 48.81; H, 5.37; N, 10.14.

Reaction of III with 2-Amino-2-methyl-1-propanol.

A solution of 5.98 g. (0.028 mole) of III in 15 ml. of dry chloroform was added with stirring to a solution of 2.5 g. (0.028 mole) of 2-amino-2-methyl-1-propanol during 0.5 hour. After standing 3 days at RT the precipitated solid was collected by suction filtration, weight 2.15 g. (37.5%), m.p. 134-138. Recrystallization from chloroform gave compound XV, m.p. 148-150°; ir: strong absorption 3350, 3150, 3000, 2900, 1600, 1470, 1350, 1210, 1140, 1080, 720 cm$^{-1}$; nmr (DMSO-$d_6$): $\delta$ 1.57 (12H singlet), $\delta$ 2.65 (3H singlet), $\delta$ 2.85 (1H broad), $\delta$ 3.68 (4H singlet, -$CH_2$-), $\delta$ 6.45 (large hump), $\delta$ 7.45 (2H doublet), $\delta$ 7.9 (2H doublet).

*Anal.* Calcd. for $C_{16}H_{29}N_3O_4S_2$: C, 49.10; H, 7.41; N, 10.74; S, 16.37. Found: C, 49.14; H, 7.49; N, 10.94; S, 16.06.

*N*-(4-Toluenesulfonyl)-*N*$^1$-(acetic acid)-urea (XVI).

A mixture of 6.15 g. (0.031 mole) of I, 2.57 g. (0.034 mole) of glycine, and 100 ml. of dry carbon tetrachloride was heated under reflux in a dry nitrogen atmosphere for 6 hours. The white solid precipitate was collected by suction filtration and washed successively with carbon tetrachloride and water. The product XVI amounted to 4.61 g. (54.7%), m.p. 190-191°; ir: 3350, 3150, 3050, 2950, 1750, 1690, 1600, 1340, 1160 cm$^{-1}$.

*Anal.* Calcd. for $C_{10}H_{12}N_2O_5S$: C, 44.11; H, 4.41; N, 10.29. Found: C, 43.80; H, 4.68; N, 10.55.

*N*-(4-Chlorobenzenesulfonyl)-*N*$^1$-(acetic acid)-urea (XVII).

Using an identical procedure to that above 4-chlorobenzenesulfonyl isocyanate (II) and glycine gave a 60.3% yield of *N*-(4-chlorobenzenesulfonyl)-*N*$^1$-(acetic acid)-urea (XVII), m.p. 178° dec.

*Anal.* Calcd. for $C_9H_9ClN_2O_5S$: C, 36.92; H, 3.08. Found: C, 37.07; H, 3.10.

*N*-(4-Toluenesulfonyl)-*N*$^1$-($\alpha$-($\beta$-phenylpropionic acid))urea (XVIII).

A mixture of 5.85 g. (0.0296 mole) of I, 4.92 g. (0.0298 mole) of phenylalanine, and 100 ml. of carbon tetrachloride was heated under reflux for 6 hours. The resulting white solid was collected by suction filtration and amounted to 2.83 g. (57.5% recovery), m.p. 274-276°; m.m.p. with phenylalanine 275-276°. Solvent from the filtrate was evaporated, leaving 4.18 g. (39%) of product XVIII, m.p. 175-178°. Recrystallization from acetone gave XVIII, with m.p. 176-178°; ir: 3325, 3100, 3000, 2900, 1720, 1670, 1550, 1340, 1160 cm$^{-1}$; nmr (perdeuterioacetone): $\delta$ 2.3 (3H singlet), $\delta$ 3.1 (2H doublet), $\delta$ 4.6 (~3H, broad), $\delta$ 7.1 (5H singlet), $\delta$ 7.25 (2H doublet) $\delta$ 7.7 (2H doublet).

*Anal.* Calcd. for $C_{17}H_{18}N_2O_5S$: C, 56.36; H, 4.97; N, 7.73. Found: C, 55.70; H, 5.29; N, 7.29.

Methyl Ester of XVI.

A solution of 2.0 g. (0.0073 mole) of XVI, 10 ml. of methanol, and 12 ml. of concentrated sulfuric acid was allowed to stand at RT for 2 hours and then poured into 100 ml. of ice water. The solid precipitate was collected and weighed 1.27 g. (60.8%), m.p. 179-185°. Recrystallization from toluene afforded pure XIX (methyl ester of XVI), m.p. 183-184°; ir: 3400, 3150, 3050, 2950, 1750, 1700, 1550, 1350, 1150 cm$^{-1}$; nmr (perdeutioacetone): $\delta$ 2.4 (3H singlet), $\delta$ 3.0 (~3H multiplet), $\delta$ 3.6 (3H singlet), $\delta$ 3.85 (2H triplet), $\delta$ 7.3 (2H doublet), $\delta$ 7.85 (2H doublet).

*Anal.* Calcd. for $C_{11}H_{14}N_2O_5S$: C, 46.14; H, 4.90; N, 9.79. Found: C, 46.22; H, 4.83; N, 9.49.

*N*-(4-Toluenesulfonyl)-*N*$^1$-(acetic acid)-thiourea (XX).

A mixture of 8.52 g. (0.04 mole) of III, 4.5 g. (0.06 mole) of glycine, and 100 ml. of dry toluene was heated under reflux 4.5 hours. White crystals of unreacted glycine were collected by suction filtration. Addition of 1 volume of petroleum ether to the filtrate produced 4.52 g. (42.7%) of white crystals, m.p. 152-154°. Recrystallization from chloroform:carbon tetrachloride followed by several recrystallizations from acetone/petroleum ether gave pure XX, m.p. 153-155°; ir: 3200, 3000 (broad), 1710, 1550, 1390, 1350, 1280, 1140 cm$^{-1}$; nmr (perdeuterioacetone): $\delta$ 2.4 (3H singlet), $\delta$ 4.4 (2H singlet), $\delta$ 7.4 (2H doublet), $\delta$ 7.9 (2H doublet), $\delta$ 8.9 (~1H, hump).

*Anal.* Calcd. for $C_{10}H_{12}N_2O_4S_2$: C, 41.65; H, 4.17; N, 9.72. Found: C, 41.57; H, 4.23; N, 9.73.

1-(4-Toluenesulfonyl)imidazolidin-5-one-2-thione (XXI).

Acid XX (0.41 g., 0.0014 mole) was added in portions to 10 ml. of cold concentrated sulfuric acid with stirring. The solution was allowed to come to RT and poured into 50 ml. of ice water. The precipitated solid was washed successively with water and petroleum ether and amounted to 0.21 g. (55.3%) of XXI, m.p. 185-190°. Recrystallization from acetone gave rod-like crystals, m.p. 196-198°; ir: 3300, 3000, 2900, 1720, 1600, 1400, 1350, 1290, 1140 cm$^{-1}$; nmr (DMSO-$d_6$): $\delta$ 2.3 (3H singlet), $\delta$ 4.3 (2H singlet, -$CH_2$-), $\delta$ 7.2 (2H doublet), $\delta$ 7.75 (2H doublet). (Dimethyl sulfoxide absorption at $\delta$ 2.4).

*Anal.* Calcd. for $C_{10}H_{10}N_2O_3S_2$: C, 44.44; H, 3.70; N, 10.37. Found: C, 44.37; H, 4.01; N, 10.47.

Methyl Ester of XX.

A portion of (0.52 g., 0.0018 mole) of XX was dissolved in 10 ml. of methanol, cooled, and mixed with 5 ml. of cold concentrated sulfuric acid. After 2.5 hours at RT the solution was added to 50 ml. of ice water. White crystals precipitated and were recrystallized from benzene to afford 0.24 g. (44%) of XXII (methyl ester of XX), m.p. 130-132°;

ir: 3300, 3000, 2900, 1750, 1550, 1380, 1350, 1290, 1140 $cm^{-1}$; nmr (perdeuterioacetone): δ 2.4 (3H singlet) δ 3.8 (3H singlet, O-$CH_3$), δ 4.4 (2H doublet, -$CH_2$-), δ 7.3 (2H doublet), δ 7.9 (2H doublet), δ 8.8 (1H, broad). (Absorption due to perdeuterioacetone exchange at δ 2.1.)

*Anal.* Calcd. for $C_{11}H_{14}N_2O_4S_2$: C, 43.69; H, 4.64; N, 9.27. Found: C, 43.45; H, 4.46; N, 9.55.

## REFERENCES AND NOTES

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(23) Some compounds were soluble only in perdeuterioacetone or DMSO-$d_6$. In those cases hydrogen exchange occurred between -NH- and/or O-H and the solvent. Some of the cyclic thioureas were too insoluble to obtain meaningful nmr spectra.