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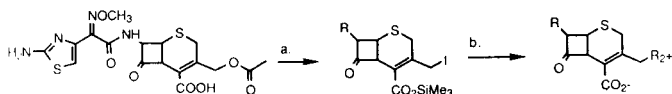
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Diethoxymethyl acetate was used to cyclize *o*-disubstituted aminopyridines to oxazolo[4,5-*c*]pyridines and imidazo[4,5-*c*]pyridines. All the possible imidazole-methylated imidazo[4,5-*c*]pyridines were prepared. A novel synthesis of 2-substituted thiazolo[5,4-*c*]pyridines and 4-amino-3-pyridinethiol was discovered.

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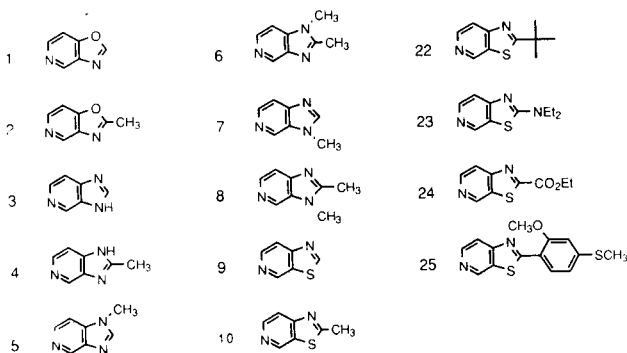
During the course of our work on cephalosporin antimicrobials we prepared the bicyclopriidines **1-10** for use as nucleophiles to displace the 3'-iodocephem in Figure 1, thereby yielding quaternary pyridinium cephalosporins [1]. This communication details preparations of the oxazolo[4,5-*c*]pyridines **1-2**, and imidazo[4,5-*c*]pyridines **3-8**. A novel synthesis of thiazolo[5,4-*c*]pyridines **9** and **10** is presented and the 2-substituted thiazolo[5,4-*c*]pyridines **22-25** were prepared to illustrate the methodology.

Figure 1



[re<sup>8</sup>] a. 1. MSTFA, methylene chloride 2. TMSI b. 1. bicyclopriidine 1-10, 22-24, acetonitrile 2. methanol

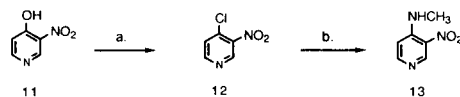
Table 1 Bicyclopriidines



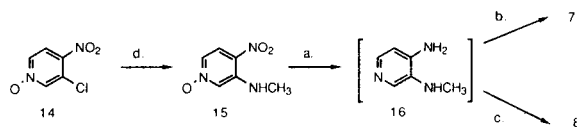
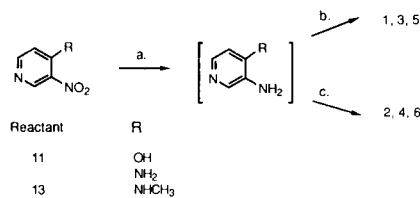
For compounds **1-8** the strategy was to prepare the required *o*-disubstituted nitropyridines then reduce to the disubstituted aminopyridines and cyclize to final product (Figure 2). The required 3-nitropyridines were readily prepared by direct nitration of 4-hydroxypyridine. Conversion of the resulting 3-nitro-4-hydroxypyridine (**11**) to **13** proceeded through the 4-chloro intermediate. Compound **14** was synthesized by nitration of 3-chloropyridine *N*-oxide. The *N*-oxide was subsequently removed concu-

rently with reduction of the 3-nitro group by catalytic hydrogenation. Stankovnik and Tisler [2] prepared **3** from 3,4-diaminopyridine by cyclization with the orthoformate-type reagent *N,N*-dimethylformamide dimethylacetal by refluxing in a high boiling co-solvent. We felt the related ester diethoxymethyl acetate would be more reactive than the amide and therefore could be used without co-solvent and for less reaction time. It proved to be a useful reagent in preparations of **1**, **3**, **5**, and **7**.

Figure 2



a.  $\text{PCl}_5$ ,  $\text{POCl}_3$   
b. methylamine, ethanol



a.  $\text{H}_2$ , Pd-C, ethanol  
b. diethoxymethyl acetate  
c. acetic anhydride  
d. methylamine, chloroform

Preparations of thiazolo[5,4-*c*]pyridines are synthetically challenging due to the positions of the nitrogen and sulfur relative to the pyridine nitrogen. Takahashi and Ueda [3] have described the synthesis of **9** and **10** by a long series of functional group transformations beginning with 4-carboxy-3-aminopyridine, but otherwise little is reported

in the literature concerning this type of compound. We attempted to synthesize **21** by the same method used to prepare **15**. Compound **14** (a 4-nitropyridine) is known and was readily converted to **15** by treatment with gaseous methylamine (Figure 2); however, when **14** was treated with thiocyanate in an attempt to introduce sulfur in the 3-position we observed evolution of nitrogen oxides and recovered a modest yield of 4-thiocyano-3-chloropyridine *N*-oxide.

Turner [4] has described the preparation of 3-lithio-4-(pivaloylamino)pyridine and its reaction with various electrophiles including dimethyl disulfide to give 4-nitrogen 3-sulfur substituted pyridines. Substitution of tetraethylthiuram disulfide for dimethyl disulfide gave dithiocarbamate **18** (Figure 3). Hydrolysis (and cyclization) of this dithiocarbamate with formic acid gave the thiazolo[5,4-*c*]pyridine **22** whereas treatment of the dithiocarbamate with sodium hydroxide gave only hydrolysis of the *N*-pivaloyl leading to **19**. Acylation of **19** with alkyl or aromatic acids gave compounds that were then readily cyclized to 2-substituted thiazolo[5,4-*c*]pyridines (Figure 4) including the target compound **10**. As mentioned above we were unable to prepare 4-amino-3-pyridinethiol (**21**) by base hydrolysis of **19**; however, Chedekel, Sharp, and Jeffrey [5]

have converted benzothiazoles to *o*-aminothiophenols using hydrazine hydrate and this method worked well for synthesis of **21** from **10**. With intermediate **21** in hand the final target compound **9** was prepared by formic acid cyclization.

## EXPERIMENTAL

Melting points were determined in glass capillaries using a Thomas-Hoover oil bath apparatus and are uncorrected. The <sup>1</sup>H-nmr spectra were determined on a GE QE-300, Bruker WM-270 or Varian T-60 and chemical shifts (δ) are reported relative to tetramethylsilane. Mass spectra were of the EI or FD (field desorption) type. Sublimations were carried out in a custom built cold-finger type apparatus by heating in an oil bath under vacuum (typically 120°/1 torr). Microanalyses were performed in sealed capsules for substances that sublime. Titrations were in 50% aqueous methanol. Flash chromatography was carried out on Merck silica-gel 60 (230-400 mesh). Thin layer chromatography was done on Merck silica-gel 60 F-254 plates. Diethoxymethyl acetate and tetraethylthiuram disulfide were obtained from Alrich Chemical Co. No attempt was made to maximize yields.

**Method 1 - General Procedure for the Reduction of Nitropyridines to Aminopyridines.**

The nitropyridine was dissolved or suspended in ethanol (20 ml/g of nitropyridine), 5% palladium on carbon (1-2 g) was added and the mixture was hydrogenated in a Parr shaker until hydrogen uptake ceased. The solution was filtered to remove catalyst, evaporated to dryness and used immediately.

**Method 2 - General Procedure for the Use of Diethoxymethyl Acetate with Aminopyridines.**

The aminopyridine was mixed with diethoxymethyl acetate (10 ml/g of aminopyridine) and heated to 110° for 4 hours. The reaction mixture was cooled and evaporated to dryness.

**Method 3 - General Procedure for the Use of Acetic Anhydride with Aminopyridines.**

The aminopyridine was mixed with acetic anhydride (10 ml/g of aminopyridine) and heated to 120° for 20 hours. It was cooled and poured into water, then stirred until all the acetic anhydride was dissolved. The solution was basified with 5*N* sodium hydroxide and extracted with diethyl ether. The extracts were washed with brine, dried over sodium sulfate, and evaporated to dryness.

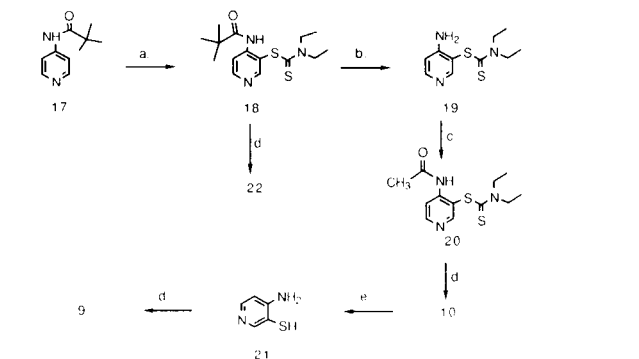
### Oxazolo[4,5-*c*]pyridine **1**.

Compound **11** [6] (15.0 g, 0.107 mole) was reduced by method 1 to give 15.1 g of viscous purple oil. This material was cyclized by method 2. The residue was stirred with ethyl acetate and decanted away from insolubles then concentrated to 14.0 g of oil and distilled 80-90°/7 torr to give 5.25 g (crystallized) mp 58-60°. Tlc (ethyl acetate, uv) indicated a single component. The product was also sublimed, 4.5 g (35%); ms: *m/e* 121 (*M* + 1); <sup>1</sup>H nmr (deuteriochloroform): 60 MHz, δ 9.3 (s, 1H), 8.7 (d, *J* = 7 Hz, 1H), 8.3 (s, 1H), 7.6 (d, *J* = 7 Hz, 1H).

### 2-Methyloxazolo[4,5-*c*]pyridine **2**.

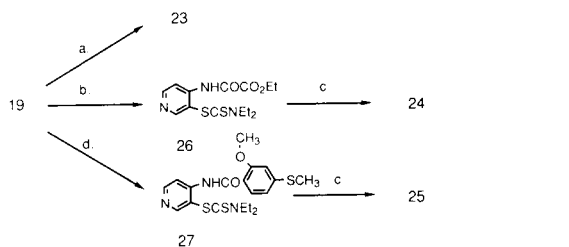
Compound **11** [6] (55 g, 0.39 mole) was hydrogenated by method 1 and cyclized by method 3 to give 20.2 g of oil that crystallized on standing; 28.1 g of crude material was sublimed to give 26.2 g (50%) mp 47-50°; ms: *m/e* 134 (*M* +); <sup>1</sup>H nmr (deu-

Figure 3



- a. 1. *n*-BuI, 2. tetraethylthiuram disulfide, THF  
 b. NaOH, ethanol  
 c. acetic anhydride, HClO<sub>4</sub>  
 d. formic acid  
 e. hydrazine hydrate, ethanol

Figure 4



- a. trifluoroacetic anhydride, THF  
 b. ethyl oxalyl chloride, Et<sub>3</sub>N, acetone  
 c. formic acid  
 d. 2-methoxy-4-methylthiobenzoic acid, DCC, CH<sub>2</sub>Cl<sub>2</sub>

teriochloroform): 60 MHz,  $\delta$  9.2 (s, 1H), 8.75 (d,  $J = 6$  Hz, 1H), 7.55 (d,  $J = 6$  Hz, 1H), 2.75 (s, 3H).

*Anal.* Calcd. for  $C_7H_6N_2O$ : C, 62.68; H, 4.51; N, 20.88. Found: C, 62.45; H, 4.50; N, 20.68.

#### 1*H*,3*H*-Imidazo[4,5-*c*]pyridine **3**.

3,4-Diaminopyridine (2.2 g, 0.02 mole) was cyclized by Method 2. The residue was sublimed to give 1.8 g (76%) mp 165-168° (lit [2] 210-215° and 170-171°); titration:  $pK_a$  5.5, 10.9; ms:  $m/e$  119 ( $M+$ );  $^1H$  nmr (DMSO- $d_6$ ): 60 MHz,  $\delta$  9.03 (s, 1H), 8.45 (s, 1H), 8.32 (d,  $J = 5$  Hz, 1H), 7.33 (d,  $J = 5$  Hz, 1H).

*Anal.* Calcd. for  $C_5H_5N_3$ : C, 60.50; H, 4.23; N, 35.27. Found: C, 60.15; H, 4.32; N, 34.94.

#### 2-Methyl-1*H*,3*H*-imidazo[4,5-*c*]pyridine **4**.

A mixture of 3,4-diaminopyridine (15.0 g, 0.13 mole) was cyclized by method 3 to give 5.8 g (34%) mp 164-166° (methanol-chloroform); titration:  $pK_a$  6.0, 11.5; ms:  $m/e$  133 ( $M+$ );  $^1H$  nmr (DMSO- $d_6$ ): 60 MHz,  $\delta$  8.88 (s, 1H), 8.42 (s, 1H), 8.33 (d,  $J = 6$  Hz, 1H), 7.57 (d,  $J = 6$  Hz, 1H), 2.6 (s, 3H).

#### 4-*N*-Methylamino-3-nitropyridine **13**.

Compound **12** [6] (28.0 g, 0.177 mole) was dissolved in ethanol (250 ml) and cooled in an ice bath, then treated for 20 minutes with a stream of gaseous methylamine. A yellow precipitate separated and was filtered and recrystallized to give 16.1 g (59%) mp 155-158° (ethanol).

*Anal.* Calcd. for  $C_6H_7N_3O_2$ : C, 47.06; H, 4.61; N, 27.44. Found: C, 47.12; H, 4.57; N, 27.68.

#### 1-Methylimidazo[4,5-*c*]pyridine **5**.

Compound **13** (7.7 g, 0.05 mole) was reduced by method 1 and the residue cyclized by method 3 to give an oil that crystallized on standing. The solid was sublimed to give 4.1 g (62%) mp 80°; ms:  $m/e$  133 ( $M+$ );  $^1H$  nmr (deuteriochloroform): 60 MHz,  $\delta$  9.15 (s, 1H), 7.97 (s, 1H), 8.5 (d,  $J = 5$  Hz, 1H), 7.37 (d,  $J = 5$  Hz, 1H), 3.87 (s, 3H).

*Anal.* Calcd. for  $C_7H_7N_3$ : C, 63.14; H, 5.30; N, 31.56. Found: C, 63.04; H, 5.42; N, 31.50.

#### 1,2-Dimethylimidazo[4,5-*c*]pyridine **6**.

Compound **13** (7.8 g, 0.051 mole) was reduced by method 1 and the residue was cyclized by method 3 to give a solid that was recrystallized to give 2.7 g (36%) mp 171-173° (ethyl acetate); ms:  $m/e$  147 ( $M+$ );  $^1H$  nmr (deuteriochloroform): 60 MHz,  $\delta$  9.0 (s, 1H), 8.4 (d,  $J = 6$  Hz, 1H), 7.2 (d,  $J = 6$  Hz, 1H), 3.7 (s, 3H), 2.6 (s, 3H).

*Anal.* Calcd. for  $C_8H_8N_3$ : C, 65.29; H, 6.16; N, 28.55. Found: C, 65.05; H, 6.14; N, 28.50.

#### *N*-Methyl-4-nitro-3-pyridineamine 1-Oxide **15**.

Compound **14** [7] (1.0 g, 5.7 mmoles) was dissolved in chloroform (10 ml) and cooled in an ice bath, then treated the solution with a stream of gaseous methylamine for 15 minutes. A precipitate separated and the reaction was diluted with ethanol, filtered and recrystallized to give 630 mg (65%) mp 228-231° (water).

*Anal.* Calcd. for  $C_6H_7N_3O_3$ : C, 42.61; H, 4.17; N, 24.84. Found: C, 42.85; H, 4.04; N, 24.67.

#### 3-Methylimidazo[4,5-*c*]pyridine **7**.

Compound **15** (14.5 g, 0.086 mole) was reduced by method 1 and cyclized by method 2. The crude product was flash chromatographed on florisil eluting with methylene chloride (discarded)

then 10% ethyl acetate-90% methylene chloride. The product containing fractions were evaporated to 8.0 g of solid and recrystallized to give 5.0 g (44%) mp 78-80° (ethyl acetate-hexanes). This material was sublimed and a sample recrystallized to give mp 98-101° (ethyl acetate, cold); ms:  $m/e$  133 ( $M+$ );  $^1H$  nmr (deuteriochloroform): 300 MHz,  $\delta$  8.95 (s, 1H), 8.45 (d,  $J = 8$  Hz, 1H), 8.1 (d,  $J = 8$  Hz, 1H), 4.0 (s, 3H).

*Anal.* Calcd. for  $C_7H_7N_3$ : C, 63.14; H, 5.30; N, 31.56. Found: C, 62.93; H, 5.22; N, 31.30.

#### 2,3-Dimethylimidazo[4,5-*c*]pyridine **8**.

Compound **15** (20.0 g, 0.163 mole) was reduced by method 1 and cyclized by method 3 to give 16.1 g of solid. The crude material was sublimed to give 3.3 g. The residue from the sublimation, believed to be the *N*-acetylaminopyridine, was not analyzed, mp 180-200°. The product was resublimed to give 2.5 g (10%) mp 144-148°; ms:  $m/e$  147 ( $M+$ );  $^1H$  nmr (deuteriochloroform): 60 MHz,  $\delta$  8.75 (s, 1H), 8.4 (d,  $J = 8$  Hz, 1H), 7.6 (d,  $J = 8$  Hz, 1H), 3.85 (s, 3H), 2.7 (s, 3H).

*Anal.* Calcd. for  $C_8H_8N_3$ : C, 65.29; H, 6.16; N, 28.55. Found: C, 65.07; H, 6.27; N, 28.72.

#### [4-[(2,2-Dimethyl-1-oxopropyl)amino]-3-pyridinyl]diethylcarbamo-dithioate **18**.

To a solution of **17** [4] (1.78 g, 10 mmoles) in tetrahydrofuran (40 ml) at -10 to 0° was added dropwise *n*-butyllithium (1.6 *M* in hexanes, 15.7 ml, 25 mmoles). A solution of tetraethylthiuram disulfide (8.88 g, 30 mmoles) in tetrahydrofuran (20 ml) was added dropwise rapidly. The reaction was allowed to reach room temperature then poured into water and extracted with ether. The extracts were washed with brine, dried over sodium sulfate and concentrated to 2.9 g of solid. This material was flash chromatographed on silica-gel, eluting with methylene chloride (discarded), then 20% ethyl acetate-80% methylene chloride. The product fractions were concentrated to solid and recrystallized to give 900 mg (28%) mp 80-82° (ethyl acetate-hexanes).

*Anal.* Calcd. for  $C_{15}H_{23}N_3S_2O$ : C, 55.35; H, 7.12; N, 12.91; S, 19.70. Found: C, 55.10; H, 6.84; N, 12.80; S, 19.64.

#### [4-Amino-3-pyridinyl]diethylcarbamo-dithioate **19**.

Compound **18** (500 mg, 1.54 mmoles) was dissolved in methanol (5 ml) and 1*N* sodium hydroxide (5 ml). It was stirred at room temperature for 2 hours then water and ethyl acetate were added. The organic layer was separated and washed with water and brine, then dried over sodium sulfate followed by concentration to a solid. It was triturated with ethyl acetate to give 135 mg (36%) mp 160-162°.

*Anal.* Calcd. for  $C_{10}H_{15}N_3S_2$ : C, 49.76; H, 6.26; N, 17.41. Found: C, 49.85; H, 6.19; N, 16.99.

#### [4-(Acetylamino)-3-pyridinyl]diethylcarbamo-dithioate **20**.

Two drops of perchloric acid were added to a solution of **19** (19.0 g, 0.079 mole) in acetic anhydride (70 ml). A pale yellow solution formed then a precipitate separated and the reaction mixture became solid. Water was added to the reaction and the mixture was stirred for 2 hours. The solid was filtered and washed with water to give 13.9 g (62%) mp 111-112°. A sample gave mp 111-113° (aqueous methanol).

*Anal.* Calcd. for  $C_{12}H_{17}N_3OS_2$ : C, 50.86; H, 6.05; N, 14.83. Found: C, 51.04; H, 6.05; N, 14.85.

#### 2-Methylthiazolo[5,4-*c*]pyridine **10**.

Compound **20** (15.6 g, 0.055 mole) was dissolved in 98% formic acid (75 ml) and heated at reflux for 4 hours. The solution was poured into ice and water and basified with 5*N* sodium hydroxide, then extracted with ether. The organic layer was washed with brine, dried over sodium sulfate and concentrated to dryness. The residue was sublimed to give 5.1 g (62%) mp 90-93° (lit [3] mp 94-95°); titration p*K*<sub>a</sub> 3.8; ms: m/e 150 (M+); <sup>1</sup>H nmr (deuteriochloroform): 60 MHz, δ 9.12 (s, 1H), 8.57 (d, J = 6 Hz, 1H), 7.85 (d, J = 6 Hz, 1H), 2.87 (s, 3H).

*Anal.* Calcd. for C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>S: C, 55.98; H, 4.03; N, 18.65. Found: C, 55.83; H, 4.19; N, 18.66.

#### Thiazolo[5,4-*c*]pyridine **9**.

A solution of **10** (400 mg, 2.7 mmoles) in 85% hydrazine hydrate (5 ml) and ethanol (5 ml) was stirred 20 hours at room temperature, then concentrated to an oil. The oil was redissolved in 98% formic acid (10 ml) and heated at reflux for 4 hours, then poured into water, made basic with 5*N* sodium hydroxide and extracted with ether. The extracts were dried over sodium sulfate, concentrated to white solid and recrystallized to give 90 mg (25%) mp 102-105° (ether-hexanes, lit [3] mp 105-106°). The solid was sublimed to give mp 104-106°; titration p*K*<sub>a</sub> 3.0; ms: m/e 136 (M+); <sup>1</sup>H nmr (deuteriochloroform): 300 MHz, δ 9.32 (s, 1H), 9.24 (s, 1H), 8.72 (d, J = 6 Hz, 1H), 8.06 (d, J = 6 Hz, 1H).

*Anal.* Calcd. for C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>S: C, 52.92; H, 2.96; N, 20.57. Found: C, 52.89; H, 2.82; N, 20.85.

#### 2-(1,1-Dimethylethyl)thiazolo[5,4-*c*]pyridine **22**.

Compound **18** (1.0 g, 3.1 mmoles) was dissolved in 98% formic acid (10 ml) and heated at reflux for 4 hours. Water was added and the solution was made basic with 5*N* sodium hydroxide, then extracted with ethyl acetate. The extracts were washed with brine and concentrated to give 520 mg oil that crystallized on standing. The solid was sublimed to give 480 mg (81%) mp 38-40°; titration p*K*<sub>a</sub> 3.4; ms: m/e 192 (M+); <sup>1</sup>H nmr (deuteriochloroform): 60 MHz, δ 9.23 (s, 1H), 8.68 (d, J = 6 Hz, 1H), 7.95 (d, J = 6 Hz, 1H), 1.57 (s, 9H).

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>S: C, 62.47; H, 6.29; N, 14.57. Found: C, 62.38; H, 6.19; N, 14.51.

#### 2-(*N,N*-Diethylamino)thiazolo[5,4-*c*]pyridine **23**.

Compound **19** (2.0 g, 8.3 mmoles) was dissolved in tetrahydrofuran (30 ml), cooled in an ice bath and trifluoroacetic anhydride (2 ml) was added over 5 minutes. The reaction was allowed to reach room temperature, then concentrated to an oil. Water was added and the mixture was extracted with ether. The acidic aqueous was made basic with 5*N* sodium hydroxide and extracted with ether. The extracts were washed with brine, dried over sodium sulfate, then concentrated to 1.12 g (65%) mp 53-56°; titration p*K*<sub>a</sub> 6.0; ms: m/e 207 (M+); <sup>1</sup>H nmr (deuteriochloroform): 60 MHz, δ 8.7 (s, 1H), 8.37 (d, J = 5 Hz, 1H), 7.33 (d, J = 5 Hz, 1H), 3.6 (q, J = 6 Hz, 4H), 1.3 (t, J = 6 Hz, 6H).

*Anal.* Calcd. for C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>S: C, 57.94; H, 6.32; N, 20.27. Found: C, 57.68; H, 6.16; N, 20.21.

#### [3-[[[(Diethylamino)thioxomethyl]thio]-4-pyridinyl]amino]oxoacetic Acid Ethyl Ester **26**.

A mixture of **19** (2.41 g, 0.01 mole), ethyl oxalyl chloride (1.4 g, 0.01 mole), triethylamine (1.1 g) and acetone (70 ml) was stirred at room temperature for 68 hours. The solid that separated was filtered and the filtrate was concentrated to a solid. Flash chromatography on silica-gel eluting first with methylene chloride

(discarded) then 15% ethyl acetate-methylene chloride yielded 1.2 g (35%) of solid. A sample gave mp 115-118° (aqueous ethanol); ms: m/e 341 (M+).

*Anal.* Calcd. for C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>: C, 49.25; H, 5.61; N, 12.31. Found: C, 49.03; H, 5.36; N, 12.18.

#### Thiazolo[5,4-*c*]pyridine-2-carboxylic Acid Ethyl Ester **24**.

A solution of **26** (0.4 g, 1.2 mmoles) in 98% formic acid (5 ml) was heated at reflux for 3 hours, then concentrated to dryness. Water was added and the mixture was extracted with ether. The extracts were washed with brine, dried over sodium sulfate and evaporated to an oil that crystallized on standing. The solid was recrystallized to give 85 mg (34%) mp 102-105° (ether-hexanes); ms: m/e 208 (M+); <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>): 270 MHz, δ 9.56 (s, 1H), 8.75 (d, J = 3 Hz, 1H), 8.20 (d, J = 3 Hz, 1H), 4.48 (q, J = 4 Hz, 2H), 1.40 (t, J = 4 Hz, 3H).

*Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S: C, 51.91; H, 3.87. Found: C, 51.68; H, 3.87.

#### [[3-[[[(Diethylamino)thioxomethyl]thio]-4-pyridinyl]amino]oxo[2-methoxy-4-(methylthio)]benzoic Acid **27**.

A solution of **19** (600 mg, 2.5 mmoles), 2-methoxy-4-methylthio-benzoic acid (495 mg, 25 mmoles), dicyclohexylcarbodiimide (515 mg, 25 mmoles) and methylene chloride (50 ml) was stirred at room temperature for 20 hours. The dicyclohexylurea that separated was removed by filtration and the filtrate was flash chromatographed on silica-gel, eluting with methylene chloride (discarded), then 10% ethyl acetate-methylene chloride. The product-containing fractions were evaporated to 435 mg (41%) mp 160-163°.

#### 2-[2-Methoxy-4-(methylthio)phenyl]thiazolo[5,4-*c*]pyridine **25**.

A solution of **27** (350 mg, 0.83 mmole) in 98% formic acid (10 ml) was heated at reflux for 2.5 hours. The cooled solution was diluted with water and basified with 5*N* sodium hydroxide, then extracted with ether. The extracts were washed with brine and dried over sodium sulfate then concentrated. The resulting solid was recrystallized to give 160 mg (67%) mp 172-177° (methanol); ms: m/e 288 (M+); <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>): 270 MHz, δ 9.36 (s, 1H), 8.6 (d, J = 5 Hz, 1H), 8.4 (d, J = 12 Hz, 1H), 7.94 (d, J = 5 Hz, 1H), 7.15 (s, 1H), 7.08 (d, J = 12 Hz, 1H), 4.14 (s, 3H), 2.62 (s, 3H).

*Anal.* Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 58.31; H, 4.19; N, 9.71. Found: C, 58.03; H, 4.43; N, 9.83.

## REFERENCES AND NOTES

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