Syntheses of 10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidines and 10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidines From Methyl Tetrahydro-4-oxo-3-thiophenecarboxylate and Methyl Tetrahydro-3-oxo-2-thiophenecarboxylate, Respectively

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A general synthesis of 10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidines and 10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidines is described. Methyl tetrahydro-4-oxo-3-thiophenecarboxylate (**13**) was condensed with 6-aminonicotinic acid (**18**) to give 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid (**19**). Treatment of **19** successively with chlorotrimethylsilane, *N*-chlorosuccinimide and water gave 10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid (**17**). Methyl tetrahydro-3-oxo-2-thiophenecarboxylate (**21**) was converted to 10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylic acid (**25**) by an analogous route.

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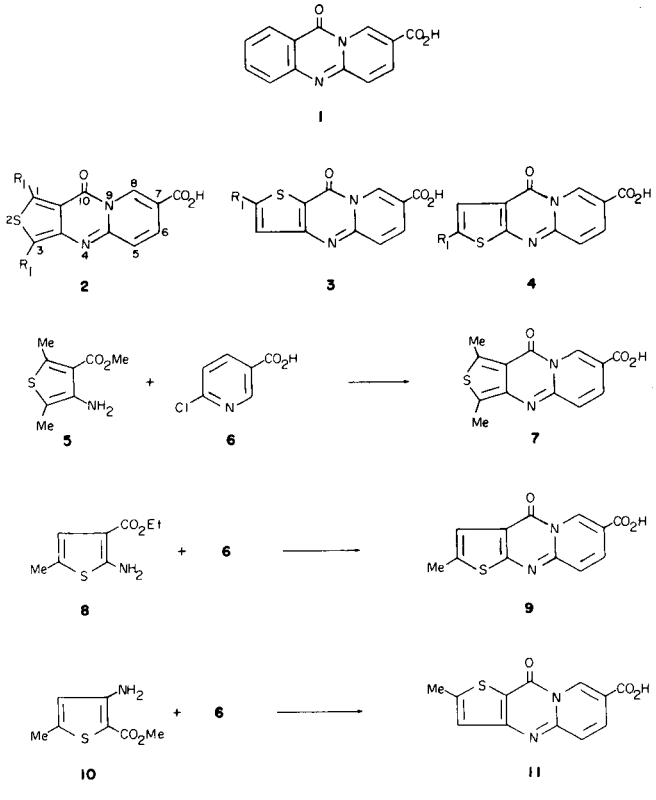
The potent oral antiallergy activity of 11-oxo-11*H*-pyrido[2,1-*b*]quinazoline-8-carboxylic acids (**1**) has been described (1,2). The synthesis and antiallergy activity of 10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidines (**2**), 10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidines (**3**) and 4-oxo-4*H*-pyrido[1,2-*a*]thieno[2,3-*d*]pyrimidines (**4**) has also been described (3,4).

In these syntheses, compounds in which R_1 is methyl were prepared by condensation of methyl 4-amino-2,5-dimethyl-3-thiophenecarboxylate (**5**), ethyl 2-amino-5-methyl-3-thiophenecarboxylate (**8**) and methyl 3-amino-5-methyl-2-thiophenecarboxylate (**10**) with 6-chloro-3-pyridine carboxylic acid (**6**) to give acids **7**, **9**, and **11** respectively (3,4). This synthesis works in all cases where R_1 is alkyl, but it is not a synthetically useful procedure when R_1 is hydrogen. The acid sensitivity of α-unsubstituted thiophenes and the vigorous acidic conditions present in the above condensations are the probable reasons for this limitation.

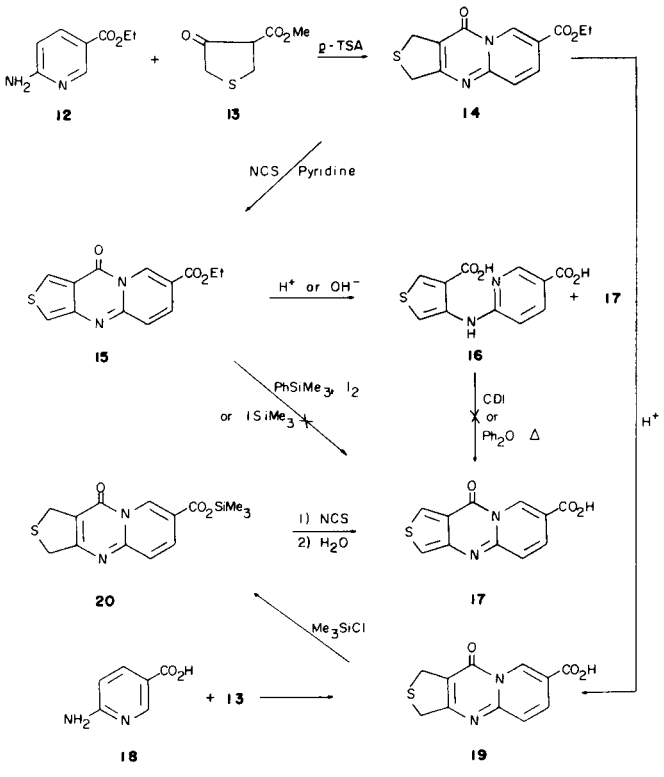
Scheme I



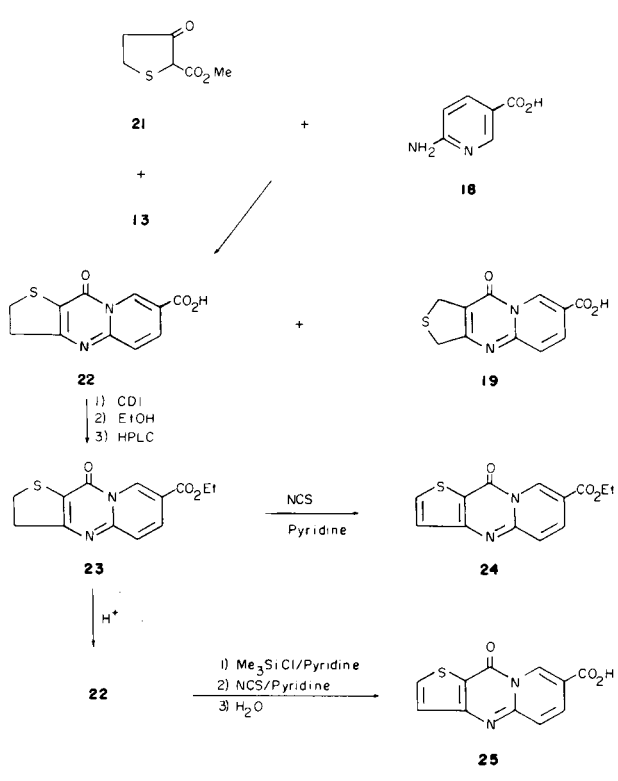
In this paper a general synthesis of these compounds is described including specific examples of types **2** and **3**. In the above syntheses, using retrosynthetic analysis, the synthons used were derived by breaking the 9,10 bond and the bond linking the 4-nitrogen to the pyridine ring. Equally useful synthons are illuminated by breaking the 9,10 bond and the bond linking the 4-nitrogen to the thiophene ring. Thus, in the second case, the 4-nitrogen is introduced *via* an aminopyridine instead of an aminothiophene. The result of this analysis is the route outlined in Scheme II, in which the acid sensitive fragment has been removed from the reactant **13** and the condensation product **14**.

Condensation of **12** with **13** (5) using acid catalysis gave **14**. Treatment of **14** with *N*-chlorosuccinimide in pyridine gave **15**. At this point it appeared to be a simple matter to convert **15** to **17**, especially as ester **14** is smoothly converted to acid **19** in refluxing 2*N* hydrochloric acid. Acid hydrolysis of ester **15** resulted in a mixture containing diacid **16**, acid **17** and other products. Alkaline hydrolysis of **15** also gave diacid **16** along with other products. Attempts to ring close **16** to **17** with 1,1'-carbonyldiimidazole (CDI) or by refluxing in diphenyl ether were unsuccessful. An attempt to convert ester **15** to acid **17** using phenyltrimethylsilane and iodine (6) gave a complex mixture. Treatment of **15** with iodotrimethylsilane (7) gave no reac-

Scheme II



Scheme III



tion.

To overcome the hydrolysis problem it was decided to aromatize acid **19**. Acid **19** was prepared by the condensation of **18** with **13** and also by the hydrolysis of ester **14**. Attempts to aromatize **19** to **17** under conditions used for the successful aromatization of **14** to **15** gave recovered starting material. This was probably due to the low solubility of **19**. This problem was overcome by converting **19** to silyl ester **20**. Ester **20** was aromatized with *N*-chlorosuccinimide in pyridine and the ester group was hydrolyzed during the aqueous work up to give the desired acid **17**. If two equivalents of *N*-chlorosuccinimide were used, a chlorine containing compound was formed in place of **17**. The structure of this compound was elucidated by comparing its ^{1}H nmr spectrum with the spectra of reference compounds. 1-Methyl-10-oxo-10*H*-pyrido[1,2-*a*]thieno-[3,4-*d*]pyrimidine-7-carboxylic acid was prepared by an unambiguous route (8). The ^{1}H nmr spectrum of this molecule in DMSO shows a singlet due to H-3 at δ 7.5. On the basis of this observation the H-1 and H-3 protons in **17** are assigned to singlets at δ 8.80 and δ 7.80 respectively. The proton attached to the thiophene ring in the chlorine containing compound appears at δ 8.73 and thus this compound is assigned the structure 3-chloro-10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid rather than the isomeric 1-chloro structure.

The synthetic route to acid **25** is outlined in scheme III. Methyl tetrahydro-3-oxo-2-thiophenecarboxylate (**21**), contaminated with **13**, was prepared by the method of Woodward, *et al.*, (9). This mixture was condensed with **18** to give a mixture of acids, **22** and **19**. The acids were converted to the corresponding esters **23** and **14**. The mixture of esters was separated by high pressure liquid chromatography to give ester **23** as a pure crystalline compound. Ester **23** was hydrolyzed with hydrochloric acid to regenerate acid **22**. Acid **22** was aromatized to **25** by the procedure used for the conversion of **19** to **17**. Treatment of ester **23** with *N*-chlorosuccinimide in pyridine gave ester **24**.

Thus the procedure outlined above constitutes a general synthesis for 10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]-pyrimidines and 10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]-pyrimidines. A report on the biological properties of these molecules will be published elsewhere.

EXPERIMENTAL

Melting points were measured with a Thomas-Hoover capillary melting point apparatus without correction. Nmr spectra were recorded on a Varian EM 390 instrument at 90 MHz with TMS as internal standard. Infrared spectra were recorded on a Beckman IR-9 or IR-7 prism grating instrument with a Digital FTS-14 interferometer. Ultraviolet spectra were recorded on a Cary Model-118 spectrophotometer. High

pressure liquid chromatographic separations were obtained using a Waters Prep-500 with silica columns.

Ethyl 3,10-Dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylate (**14**).

Ethyl 6-aminonicotinate (2.5 g, 0.015 mole), methyl tetrahydro-4-oxo-3-thiophenecarboxylate (**13**) (6.2 g, 0.039 mole) and *p*-toluenesulfonic acid monohydrate (0.25 g) were thoroughly mixed and heated at 155-160° under nitrogen for 90 minutes. The distillate was collected in a Dean-Stark trap. The residue was cooled, triturated with boiling ethanol and filtered. Recrystallization from methanol gave ethyl 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylate (1.2 g, 30%), mp 183-185°; uv (methanol): λ max 235 (20,400) and 347 (11,400); ir (potassium bromide): 1722 and 1700 cm^{-1}; nmr (deuteriochloroform): δ 9.55 (d, 1, ArH), 8.20 (dd, 1, ArH), 7.56 (d, 1, ArH), 4.45 (q, 2, CH_2), 4.29 (s, 4, CH_2S), and 1.46 (t, 3, CH_3).

Anal. Calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14; S, 11.60. Found: C, 56.51; H, 4.67; N, 10.08; S, 11.76.

Ethyl 10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylate (**15**).

A mixture of ethyl 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]-pyrimidine-7-carboxylate (**14**) (2.0 g, 0.0072 mole) and *N*-chlorosuccinimide (0.97 g, 0.0072 mole) in pyridine (20 ml) was heated on a steam bath for 18 minutes. The reaction mixture was cooled and poured into a large volume of ice-water. The precipitate was filtered, washed with water and dried. Recrystallization from ethanol gave ethyl 10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylate (1.1 g, 55%) mp 175-176°; uv methanol λ max 263 (29,600), 317 (10,600), 332 (10,900), 345 (7,550) and 400 (2,740); ir (potassium bromide): 1735 cm^{-1}; nmr (deuteriochloroform): δ 9.33 (d, 1, ArH), 8.52 (d, 1, ArH), 7.71 (dd, 1, ArH), 7.55 (d, 1, ArH), 7.15 (d, 1, ArH), 4.42 (q, 2, CH_2) and 1.42 (t, 3, CH_3).

Anal. Calcd. For $C_{13}H_{10}N_2O_3S$: C, 56.92; H, 3.67; N, 10.21; S, 11.69. Found: C, 56.64; H, 3.78; N, 10.08; S, 11.76.

3,10-Dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic Acid (**19**).

A suspension of ethyl 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno-[3,4-*d*]pyrimidine-7-carboxylate (**14**) (0.25 g, 0.001 mole) in 2*N* hydrochloric acid (5 ml) was refluxed for 2.5 hours. The reaction mixture was cooled. The product was filtered, washed with water and dried. Recrystallization from dimethylformamide gave 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid (0.14 g, 62%), mp 311-312°; uv (methanol): λ max 233 (18,400) and 345 (11,200) ir (potassium bromide) 1720 cm^{-1}; nmr (trifluoroacetic acid): δ 10.04 (d, 1, ArH), 9.03 (dd, 1, ArH), 8.19 (d, 1, ArH), 4.61 (m, 2, CH_2S) and 4.38 (m, 2, CH_2S).

Anal. Calcd. for $C_{11}H_8N_2O_3S$: C, 53.22; H, 3.25; N, 11.28; S, 12.92. Found: C, 53.16; H, 3.35; N, 11.28; S, 13.03.

3,10-Dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic Acid (**19**) From 6-Aminonicotinic Acid.

6-Aminonicotinic acid (10 g, 0.072 mole), methyl tetrahydro-4-oxo-3-thiophenecarboxylate (**13**) (28 g, 0.175 mole) and *p*-toluenesulfonic acid monohydrate (1.0 g) were thoroughly mixed and heated at 170° under nitrogen for 75 minutes. The distillate was collected in a Dean-Stark trap. The residue was cooled, triturated with boiling chloroform and filtered to give the product. Recyrstallization from dimethylformamide gave 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid (11.3 g, 63%), mp 314-315°.

10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic Acid (**17**).

Chlorotrimethylsilane (2.6 ml, 0.02 mole) was added to an ice-cold solution of 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid (**19**) (5.0 g, 0.02 mole) in pyridine (40 ml) under nitrogen. The mixture was stirred at ice-bath temperature for one hour and then allowed to warm to room temperature. *N*-Chlorosuccinimide (2.74 g, 0.02 mole) was added and the mixture was heated at 90-95° for 20 minutes. The mixture was cooled, diluted with water and stirred for 15 minutes. The precipitate was filtered, dried and washed with boiling acetone (3 × 100 ml). Recrystallization from dimethylformamide gave 10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid (3.9 g, 79%), mp 320° dec; uv (methanol): λ max 223 (23,900), 261 (35,400), 330 (8,300) and 400 (3,700); ir (potassium bromide) 1715 cm^{-1}; nmr (DMSO): δ 9.05 (d, 1, ArH), 8.80 (d, 1, ArH), 7.80 (d, 1, ArH), 7.65 (dd, 1, ArH) and 7.15 (d, 1, ArH).

Anal. Calcd. for $C_{11}H_6N_2O_3S$: C, 53.65; H, 2.46; N, 11.38; S, 13.02. Found: C, 53.43; H, 2.67; N, 11.50; S, 13.04.

3-Chloro-10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic Acid.

Chlorotrimethylsilane (0.4 ml, 0.003 mole) was added to an ice-cold solution of 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid (0.75 g, 0.003 mole) in pyridine (5 ml) under nitrogen. The mixture was stirred at ice-bath temperature for one hour and then allowed to warm to room temperature. *N*-Chlorosuccinimide (0.8 g, 0.006 mole) was added and the mixture was heated at 95° for 20 minutes. The mixture was cooled, diluted with water and stirred for 15 minutes. The precipitate was filtered and dried. Recrystallization from ethanol gave 3-chloro-10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid (0.5 g, 51%), mp 285° dec; uv (methanol): λ max 224 (26,600), 263 (41,000), 289 (14,300), 366 (12,400) and 412 (4,380); ir (potassium bromide): 1730 cm^{-1}; nmr (dimethylsulfoxide): δ 9.03 (d, 1, ArH), 8.73 (s, 1, ArH), 7.72 (dd, 1, ArH) and 7.25 (d, 1, ArH).

Anal. Calcd. for $C_{11}H_5ClN_2O_3S$·EtOH: C, 47.78; H, 3.39; N, 8.57; Cl, 10.85; S, 9.81. Found: C, 48.02; H, 3.44; N, 8.65; Cl, 11.03; S, 9.55.

3,10-Dihydro-10-oxo-2*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylic Acid (**22**) and 3,10-Dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno-[3,4-*d*]pyrimidine-7-carboxylic Acid (**19**).

6-Aminonicotinic acid (7.3 g, 0.053 mole), methyl tetrahydro-3-oxo-2-thiophenecarboxylate (**21**) (contaminated with methyl tetrahydro-4-oxo-3-thiophenecarboxylate) (27.6 g, 0.140 mole) and *p*-toluenesulfonic acid monohydrate (0.7 g) were thoroughly mixed and heated at 170° under nitrogen for 75 minutes. The distillate was collected in a Dean-Stark trap. The residue was cooled, triturated with boiling chloroform and filtered to give a mixture of **19** and **22** as a yellow powder (10.4 g, 79%).

Ethyl 3,10-Dihydro-10-oxo-2*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylate (**23**) and Ethyl 3,4-Dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno-[3,4-*d*]pyrimidine-7-carboxylate (**14**).

A mixture of 3,10-dihydro-10-oxo-2*H*-pyrido[1,2-*a*]thieno[3,2-*d*]-pyrimidine-7-carboxylic acid (**22**) (containing 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylic acid) (10.4 g, 0.042 mole) and carbonyldiimidazole (6.9 g, 0.042 mole) in dimethylformamide (10 ml) and tetrahydrofuran (500 ml) was refluxed with stirring for 3 hours. Absolute ethanol (20 ml) was added and refluxing was continued for a further 3 hours. The solvents were removed under reduced pressure to give a solid product (mixture of **14** and **23**).

The mixture was dissolved in a minimum amount of chloroform and fractionated by high pressure liquid chromatography using ethyl acetate as solvent. Fraction I was recrystallized from isopropyl ether-2-propanol to give ethyl 3,10-dihydro-10-oxo-2*H*-pyrido[1,2-*a*]thieno[3,2-*d*]-pyrimidine-7-carboxylate (5.3 g, 46%), mp 155-156°; uv (methanol): λ max 265 (19,200) and 378 (10,600); ir (potassium bromide): 1725 and 1697 cm^{-1}; nmr (deuteriochloroform): δ 9.61 (d, 1, ArH), 8.09 (dd, 1, ArH), 7.54 (d, 1, ArH), 4.47 (q, 2, CH_2), 3.47 (s, 4, CH_2CH_2) and 1.45 (t, 3, CH_3).

Anal. Calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14; S, 11.60. Found: C, 56.32; H, 4.42; N, 10.11; S, 11.62.

Fraction II was recrystallized from methanol to give ethyl 3,10-dihydro-10-oxo-1*H*-pyrido[1,2-*a*]thieno[3,4-*d*]pyrimidine-7-carboxylate (0.5 g, 4%), mp 183-185°.

Ethyl 10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylate (**24**).

Ethyl 10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylate (**24**).

A mixture of ethyl 3,10-dihydro-10-oxo-2*H*-pyrido[1,2-*a*]thieno[3,2-*d*]-pyrimidine-7-carboxylate (**23**) (0.4 g, 0.0014 mole) and *N*-chlorosuccinimide (0.9 g, 0.0014 mole) in pyridine (4 ml) was heated on a steam bath for 18 minutes. The reaction mixture was cooled and poured into a large volume of ice-water. The precipitate was filtered, washed with water and dried. Recrystallization from ethanol gave ethyl 10-oxo-10*H*-pyrido-[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylate (0.2 g, 53%), mp 188-190°; uv (methanol): λ max 252 (27,700) and 350 (12,700); ir (potassium bromide): 1725 and 1695 cm^{-1}; nmr (deuteriochloroform): δ 9.66 (d, 1, ArH), 8.2-7.9 (m, 2, ArH), 7.65-7.25 (m, 2, ArH), 4.44 (q, 2, CH_2) and 1.43 (t, 3, CH_3).

Anal. Calcd. for $C_{13}H_{10}N_2O_3S$: C, 56.92; H, 3.67; N, 10.21; S, 11.69. Found: C, 56.74; H, 3.64; N, 10.16; S, 11.68.

3,10-Dihydro-10-oxo-2*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylic Acid (**22**).

A suspension of ethyl 3,10-dihydro-10-oxo-2*H*-pyrido[1,2-*a*]thieno-[3,2-*d*]pyrimidine-7-carboxylate (**23**) (5.0 g, 0.018 mole) in 2*N* hydro chloric acid (60 ml) was refluxed for 3 hours. The reaction mixture was cooled in an ice-bath. The precipitate was filtered, washed with water, with acetone and dried to give 3,10-dihydro-10-oxo-2*H*-pyrido-[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylic acid (3.5 g, 78%), mp 325° dec; uv (methanol): λ max 265 (19,200) and 378 (10,600); ir (potassium bromide): 1710 cm^{-1}; nmr (trifluoroacetic acid): δ 9.97 (d, 1, ArH), 8.89 (dd, 1, ArH), 8.16 (d, 1, ArH) and 3.75 (m, 4, $-CH_2CH_2-$).

Anal. Calcd. for $C_{11}H_8N_2O_3S$: C, 53.22; H, 3.25; N, 11.28; S, 12.92. Found: C, 53.22; H, 3.41; N, 11.13; S, 12.98.

10-Oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylic Acid (**25**).

Chlorotrimethylsilane (2.35 ml, 0.08 mole) was added to an ice-cold solution of 3,10-dihydro-10-oxo-2*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylic acid (**22**) (4.5 g, 0.018 mole) in pyridine (35 mls) under nitrogen. The mixture was stirred at ice-bath temperature for one hour and then allowed to warm to room temperature. *N*-Chlorosuccinimide (2.44 g, 0.018 mole) was added and the mixture was heated at 95° for 20 minutes. The mixture was cooled, diluted with water (5 ml) and stirred for 15 minutes. The precipitate was filtered, washed with boiling acetone and dried to give 10-oxo-10*H*-pyrido[1,2-*a*]thieno[3,2-*d*]pyrimidine-7-carboxylic acid (3.5 g, 78%), mp 335° dec; uv (methanol): λ max 221 (17,200), 250 (27,000), 352 (13,300) and 368 (11,400); ir (potassium bromide): 1717 cm^{-1}; nmr (trifluoroacetic acid): δ 10.20 (d, 1, ArH), 9.0 (dd, 1, ArH), 8.53 (d, 1, ArH), 8.23 (d, 1, ArH) and 7.63 (d, 1, ArH).

Anal. Calcd. for $C_{11}H_6N_2O_3S$: C, 53.65; H, 2.46; N, 11.38; S, 13.02. Found: C, 53.42; H, 2.83; N, 11.52; S, 12.70.

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