

Synthesis of 5*H*-Pyrido[1,2-*a*]pyrimido[5,4-*e*]pyrimidin-5-ones and
5*H*-Pyrido[1,2-*a*]pyrimido[4,5-*d*]pyrimidin-5-ones and
Rearrangement of the Former to the Latter

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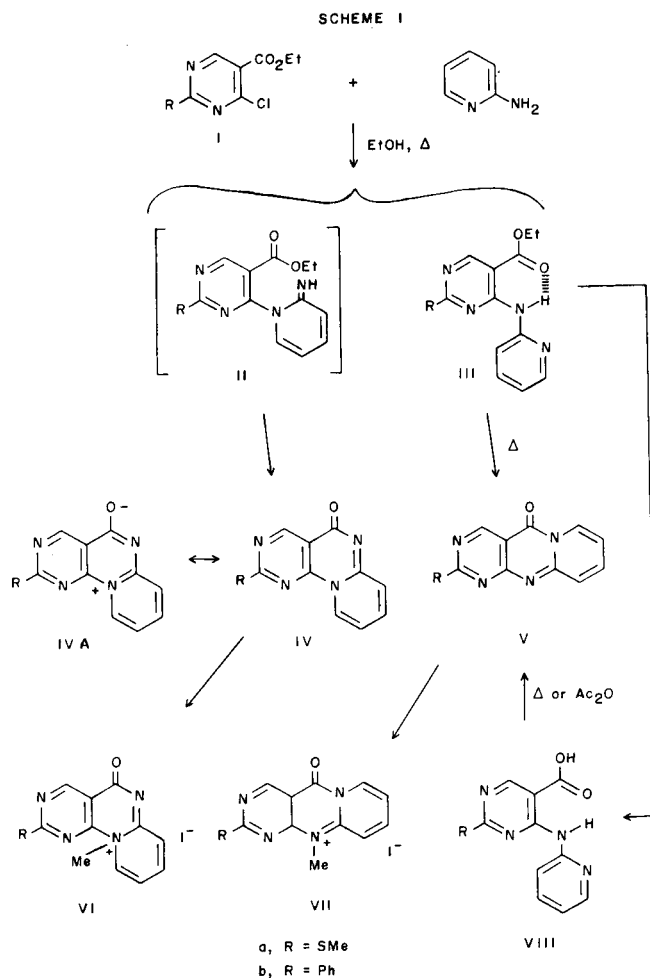
5*H*-Pyrido[1,2-*a*]pyrimido[5,4-*e*]pyrimidin-5-ones IVa,b and 5*H*-pyrido[1,2-*a*]pyrimido[4,5-*d*]pyrimidin-5-ones Va,b were synthesized from ethyl 4-chloro-5-pyrimidinecarboxylate and 2-aminopyridine. The former compounds were obtained directly upon heating the reactants in ethanol, and the latter were prepared by the fusion of ethyl 4-(2-pyridylamino)-5-pyrimidinecarboxylates obtained as minor products from the above reaction. The angular fused cyclic compounds, IVa,b were rearranged to the linear tricycles, Vb-f upon heating with amines.

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Previously, we reported the syntheses of a variety of novel nitrogen heterocycles starting with ethyl 2-substituted-4-chloro-5-pyrimidinecarboxylates I [1a-g]. This paper describes the preparation of 5*H*-pyrido[1,2-*a*]pyrimido[5,4-*e*]pyrimidin-5-ones and 5-*H*-pyrido[1,2-*a*]pyrimido[4,5-*d*]pyrimidin-5-ones from I. Furthermore, it reports the molecular rearrangements of the former angular tricycles to the latter linear isomers.

Treatment of ethyl 4-chloro-2-methylthio-5-pyrimidinecarboxylate (Ia) with 2-aminopyridine in refluxing ethanol afforded two products: one (mp 313° dec) that was separated from the hot reaction mixture and 2-(methylthio)-4-(2-pyrimidylamino)-5-pyrimidinecarboxylic acid ethyl ester (IIIa) which was precipitated upon cooling the reaction mixture. Compound IIIa showed infrared absorption bands at 1704 and 3226 cm⁻¹ ascribable to a hydrogen bonded ester carbonyl and an amino NH stretching, respectively. Alkaline hydrolysis produced the corresponding carboxylic acid (VIIIa). When fused neat, IIIa was transformed to a high melting compound (mp 223-225°) with elimination of ethanol. The same compound was obtained from the acid, VIIIa by treatment with boiling acetic anhydride. On the basis of analogies with similar reactions [2,3] and the result of elemental analysis the new product obtained by the fusion of IIIa or by the cyclization of VIIIa is thought to be the linear tricyclic 2-(methylthio)-5*H*-pyrido[1,2-*a*]pyrimido[4,5-*d*]pyrimidin-5-one (Va). The tricycle Va showed its infrared carbonyl absorption band at 1724 cm⁻¹.

The result of elemental analysis of the initial precipitate (mp 313° dec) indicated it to be an isomer of Va: the angular tricycle 2-(methylthio)-5*H*-pyrido[1,2-*a*]pyrimido[5,4-*e*]pyrimidin-5-one (IVa) was assigned for the structure. Discussion in support of the assignment is presented below. Unlike Va, IVa showed a carbonyl absorption band at 1650 cm⁻¹ in its infrared spectrum, indicating that the

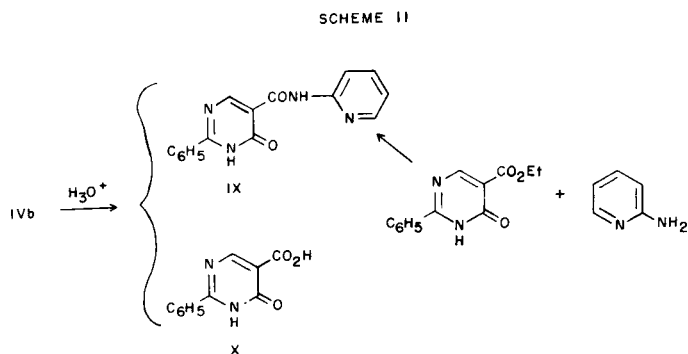


compound exists predominantly as a zwitter ionic form. However, the *N*-methyl derivative VIa formed by the reaction of IVa with methyl iodide exhibited a strong infrared absorption band at 1724 cm⁻¹. The analogous treatment of Ib with 2-aminopyridine afforded IVb and pyrimidine-

carboxylic acid ester IIIb which cyclized to give Vb upon fusion.

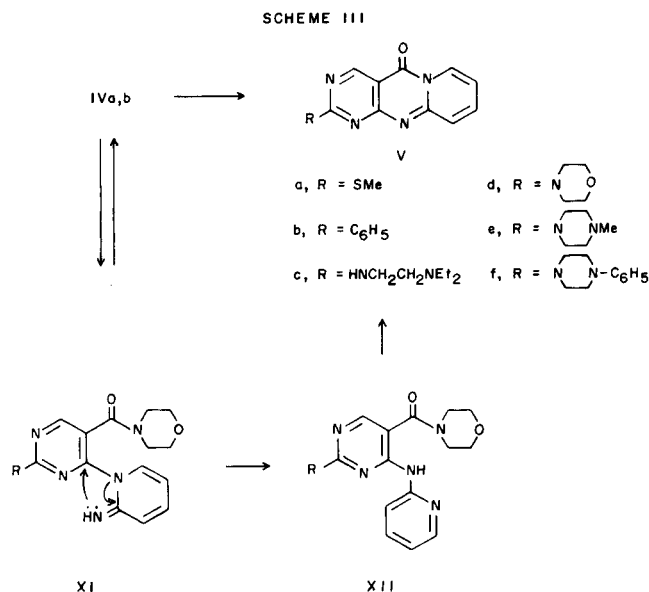
Depending on the type of substrate and reaction conditions such as solvent and temperature, 2-aminopyridine is known to give two different products: one derived from the ring nitrogen, and one from the 2-amino group. Reportedly, the reaction of 2-aminopyridine with alkyl halide occurs predominantly at the ring nitrogen [5,6]. Accordingly, IIa is the expected major product from the reaction of the aminopyridine with Ia. Under the reaction conditions, IIa thus formed undergoes an internal cyclization to give IVa. In support of the formation of IVa, Gupta, *et al.* reported that an analogous reaction of 2-aminopyridine with methyl 2-chloro-3,5-dinitrobenzoate in refluxing ethanol gave 8,10-dinitro-5*H*-pyrido[1,2-*a*]quinazolin-5-one [7]. On the other hand, IIIa formed from the reaction of the exocyclic nitrogen failed to cyclize, presumably due to the intramolecular hydrogen bonding occurring between the 2-amino proton and the neighboring carbethoxy carbonyl group. Such hydrogen bonding leads the molecule to assume a configuration which is unfavorable for the cyclization reaction. Consequently, vigorous conditions such as fusion were required for the ring closure reaction of III to occur. A similar explanation was proposed previously for the unsuccessful cyclization of ethyl 4-(2-hydroxyethylamino)-2-phenyl-5-pyrimidinecarboxylate [1c].

Study of acid hydrolysis of IVb provided additional evidence for the structural assignments (Scheme II). The treatment of IVb with dilute hydrochloric acid under refluxing conditions gave 1,6-dihydro-6-oxo-2-phenyl-*N*-(2-pyridyl)-5-pyrimidinecarboxamide (IX) as the major product along with 1,6-dihydro-6-oxo-2-phenylpyrimidine-5-carboxylic acid (X). The structure of IX was proven by an independent synthesis which involved reaction of ethyl 4-hydroxy-5-pyrimidinecarboxylate with 2-aminopyridine.



Treatment of Va with boiling morpholine for 2 hours afforded 2-(4-morpholino)-5*H*-pyrido[1,2-*a*]pyrimido[4,5-*d*]pyrimidin-5-one (Vd) in 80% yield. The similar treatment of Va with 2-diethylaminoethylamine for 10 minutes afforded 2-(2-diethylaminoethylamino)-5*H*-pyrido[1,2-*a*]pyrim-

ido[4,5-*d*]pyrimidin-5-one (Vc) and *N*-(2-diethylaminoethyl)-2-(diethylaminoethyl)amino-4-(2-pyridinylamino)-5-pyrimidinecarboxamide in 24% and 20% yields, respectively. However, when IVa was treated similarly with boiling morpholine, the product that was obtained in a quantitative yield was not anticipated 2-morpholino derivative of IV but instead Vd. Similar ring transformations also occurred when IVa was treated with *N,N*-diethylethylenediamine, 1-methylpiperazine and 1-phenylpiperazine, giving Vc, Ve, and Vf, respectively (Scheme III).



An explanation for the ring transformation involves an initial ring cleavage of IVa, presumably with a concurrent displacement of the methylthio group, both by the amine used, giving an imidopyridinylpyrimidine intermediate such as XI. Under the reaction conditions, the imidinopyridinyl moiety of the intermediate undergoes a Smiles type rearrangement to give a sterically less crowded pyridinyl-amino derivative. The cyclization of the latter intermediate would yield the linear tricycle V. In support of the proposed mechanism, when IVb was refluxed with morpholine for 1 hour, there was obtained 4-[[2-phenyl-4-(2-pyridinylamino)-5-pyrimidinyl]carbonyl]morpholine (XII) which was cyclized by fusion, giving Vb (Scheme III).

EXPERIMENTAL

Melting points were taken in capillary tubes (Thomas-Hoover melting point apparatus) and are uncorrected. The ir spectra were obtained in potassium bromide pellets using a Perkin-Elmer 21 spectrophotometer. The uv absorption spectra were obtained in ethanol solution with a Perkin-Elmer Model 450 UV-visible spectrophotometer. The nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as the internal reference. Combustion elemental analyses were performed by the Analytical Section of these Laboratories. The reported yields may be improved under optimal reaction conditions.

Reaction of 4-Chloro-2-methylthio-5-pyrimidinecarboxylic Acid Ethyl Ester (Ia) with 2-Aminopyridine to Yield 2-(Methylthio)-5H-pyrido[1,2-a]pyrimido[5,4-e]pyrimidin-5-one (IVa) and 2-(Methylthio)-4-(2-pyridylamino)-5-pyrimidinecarboxylic Acid Ethyl Ester (IIIa).

A mixture of Ia (35 g), 2-aminopyridine (30 g), and ethanol (750 ml) was heated under reflux for 21 hours. A precipitate separated during the reflux period. The hot reaction mixture was filtered, and the filter residue was washed with hot ethanol, giving 18.6 g (51%) of IVa, mp 313° dec; uv: 217 (24900), 249 (17900), 279 (27000) and 338 m μ (6700).

Anal. Calcd. for C₁₁H₈N₄O₂S: C, 54.10; H, 3.30; N, 22.94. Found: C, 54.11; H, 3.27; N, 23.13.

The combined filtrate and washings were allowed to stand at room temperature overnight. The precipitate that separated was collected on a filter, and washed with ethanol, to give 14 g (32%) of IIIa, mp 142-144°; nmr (deuteriochloroform): 1.40 (t, 3H, CH₃), 2.60 (s, 3H, SCH₃), 4.45 (q, 2H, CH₂), 6.95-8.90 (m, 5H), and 10.85 (s, 1H, NH).

Anal. Calcd. for C₁₃H₁₄N₄O₂S: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.44; H, 4.94; N, 19.45.

Reaction of 4-Chloro-2-phenyl-5-pyrimidinecarboxylic Acid Ethyl Ester (Ib) and 2-Aminopyridine to Yield 2-Phenyl-5H-pyrido[1,2-a]pyrimido[5,4-e]pyrimidin-5-one (IVb) and 2-Phenyl-4-(pyridylamino)-5-pyrimidinecarboxylic Acid Ethyl Ester (IIIb).

A mixture of Ib (13.5 g), 2-aminopyridine (10.5 g), and ethanol (200 ml) was heated under reflux for 26 hours, then filtered while hot. The filter residue was washed with ethanol to give 4.65 g (33%) of IVb, mp 280-282° dec; uv: 219 (2.99 × 10⁴), 253 (2.24 × 10⁴), 280 (2.33 × 10⁴) 297 (2.27 × 10⁴), and 368 (0.59 × 10⁴).

Anal. Calcd. for C₁₆H₁₀N₄O₂: C, 70.06; H, 3.68; N, 20.43. Found: C, 69.90; H, 3.81; N, 20.20.

Chilling of the combined filtrate and washings caused separation of IIIb which was collected on a filter, and recrystallized from ethanol, yield 1.4 g (85%); mp 138-140°; ir: 1695 cm⁻¹ (CO); uv: 278 (3.38 × 10⁴), 290 (3.77 × 10⁴), and 330 m μ (0.72 × 10⁴).

Anal. Calcd. for C₁₈H₁₆N₄O₂: C, 67.48; H, 5.03; N, 17.49. Found: C, 67.25; H, 5.02; N, 17.57.

2-Methylthio-4-(2-pyridylamino)-5-pyrimidinecarboxylic Acid (VIIIa).

A mixture of IIIa (4.5 g), 15% aqueous sodium hydroxide solution (70 ml), and ethanol (30 ml) was heated under reflux for 1 hour. After the reaction mixture was cooled, it was acidified with concentrated hydrochloric acid. The precipitate that separated was collected on a filter, and purified by dissolution in water with addition of a small amount of dilute sodium hydroxide solution, filtration, and acidification with dilute hydrochloric acid, giving 3.8 g (93%) of the product, mp 239°; ir: 1680 cm⁻¹ (CO); uv: 277 (shoulder) (2.41 × 10⁴) and 293 m μ (2.61 × 10⁴).

Anal. Calcd. for C₁₁H₁₀N₄O₂S: C, 50.38; H, 3.84; N, 21.37. Found: C, 50.54; H, 3.90; N, 21.48.

2-Phenyl-4-(2-pyridylamino)-5-pyrimidinecarboxylic Acid (VIIIb).

A mixture of IIIb (0.5 g), 15% aqueous sodium hydroxide solution (30 ml), and ethanol (10 ml) was heated under reflux for 1 hour. Chilling of the reaction mixture caused separation of a precipitate which was collected on a filter. The filter residue was dissolved in a small amount of hot water, and the aqueous solution was filtered. Acidification of the filtrate with dilute hydrochloric acid caused separation of a precipitate which was collected on a filter and washed with water several times, mp 245-247° dec.

Anal. Calcd. for C₁₆H₁₂N₄O₂: C, 65.76; H, 4.14; N, 19.17. Found: C, 65.38; H, 4.28; N, 19.10.

2-(Methylthio)-5H-pyrido[1,2-a]pyrimido[4,5-d]pyrimidin-5-one (Va).

A. From IIIa.

A flask containing IIIa (2.5 g) was heated in an oil bath at 240° for 25 minutes. The solid mass that was obtained was crushed using a mortar and pestle, and recrystallized from dimethylformamide, giving 1.8 g

(86%) of the product, mp 223-225°; uv: 236 (1.10 × 10⁴), 242 (0.98 × 10⁴), 282 (2.68 × 10⁴), 295 (2.52 × 10⁴), 306 (2.57 × 10⁴), 355 (0.9 × 10⁴), and 370 (0.98 × 10⁴).

Anal. Calcd. for C₁₁H₈N₄O₂S: C, 54.10; H, 3.30; N, 22.94. Found: C, 53.96; H, 3.39; N, 23.09.

B. From VIIIa and Acetic Anhydride.

A mixture of VIIIa (0.8 g) and acetic anhydride (25 ml) was heated under reflux for 2 hours, and chilled in ice. A precipitate was collected on a filter and washed with ethanol, giving 0.65 g (88%) of Va which is identical with that prepared by the Method A (mixture mp and ir).

C. From VIIIa by Fusion.

Compound VIIIa (1.5 g) was fused neat in an oil bath (240°) for 25 minutes. The solid mass that was obtained was ground to powder, and recrystallized from dimethylformamide, giving 1.2 g (95%) of Va.

2-Phenyl-5H-pyrido[1,2-a]pyrimido[4,5-d]pyrimidin-5-one (Vb).

A. From IIIb.

Compound IIIb (0.2 g) was fused neat at 250° (oil bath temperature) for 15 minutes. The solid mass that was obtained was recrystallized from dimethylformamide, giving Vb, mp 262-264°; ir: 1715 cm⁻¹ (CO); uv: 235.5 (1.15 × 10⁴), 241 (1.17 × 10⁴), 278 (shoulder) (2.28 × 10⁴), 295 (3.05 × 10⁴), and 3.50 m μ (0.98 × 10⁴).

Anal. Calcd. for C₁₆H₁₀N₄O: C, 70.06; H, 3.68; N, 20.43. Found: C, 69.70; H, 3.96; N, 20.74.

B. From 4-[2-Phenyl-4-(2-pyridinylamino)-5-pyrimidinyl]carbonylmorpholine (XII).

One half g of XII was fused in an oil bath maintaining the temperature of 200° for 3 hours. The solid mass was then recrystallized from dimethylformamide, giving 0.25 g (66%) of Vb, mp 263-265°.

Hydrolysis of IVb.

A mixture of IVb (3.0 g) and hydrochloric acid (1N, 250 ml) was heated under reflux for 3 hours. Chilling of the reaction mixture in ice caused separation of a precipitate which was collected on a filter and washed with water, then with ethanol. Recrystallization of the crude product from pyridine afforded 1,6-dihydro-6-oxo-2-phenyl-N-(2-pyridyl)-5-pyrimidinecarboxamide (IX), mp 305-307° dec. Another purification by dissolution in dilute aqueous sodium hydroxide solution and precipitation by acidification with dilute hydrochloric acid improved the mp to 313-315°, yield, 21 g (58%); ir: 1686 cm⁻¹ (CO); uv: 244 (1.53 × 10⁴), and 3.23 m μ (2.00 × 10⁴).

Anal. Calcd. for C₁₆H₁₂N₄O₂: C, 65.75; H, 4.14; N, 19.17. Found: C, 65.75; H, 4.21; N, 19.13.

Evaporation of the pyridine mother liquor on a rotary evaporator afforded a solid residue which was treated with dilute aqueous sodium hydroxide solution, and filtered. Acidification of the filtrate with dilute hydrochloric acid caused separation of a precipitate which was collected on a filter and washed with water. Purification by dissolution in dilute aqueous sodium hydroxide followed by precipitation by acidification with dilute hydrochloric acid gave 0.2 g (8.5%) of 1,6-dihydro-6-oxo-2-phenylpyrimidine-5-carboxylic acid (X), mp 270-272° dec [8], lit mp 280-281° [9], 214° [10]; ir: 3030-2300 and 1742 (CO₂H), and 1640 cm⁻¹ (amide CO).

Anal. Calcd. for C₁₁H₈N₂O₃: C, 61.11; H, 3.73; N, 12.96. Found: C, 61.43; H, 3.60; N, 13.35.

4-Hydroxy-2-phenyl-N-(2-pyridyl)-5-pyrimidinecarboxamide (IX).

A mixture of 4-hydroxy-2-phenyl-5-pyrimidinecarboxylic acid ethyl ester (3.5 g) and 2-aminopyridine (10 g) was sealed in a steel autoclave. The autoclave was heated in an oil bath maintaining the temperature of 230° for 5 hours. After being cooled, the autoclave was opened, and the black semisolid material was extracted with warm dimethylformamide. The extract was diluted with water, and extracted with ether several times. The combined ether extracts were washed with water, then dried

with magnesium sulfate. Evaporation of ether afforded a mixture of a solid and an oil. The solid was collected on a filter, washed with ethanol, and recrystallized from dimethylformamide, mp 311-312°. Mixture mp with IX obtained by hydrolysis of IVb was not depressed.

Reaction of Va with 2-Diethylaminoethylamine.

A mixture of Va (1.0 g) and 2-diethylaminoethylamine (15 ml) was heated under reflux for 10 minutes, then chilled in ice to cause separation of a precipitate. The precipitate was collected on a filter and washed with ethanol giving 0.3 g (24%) of 2-(2-diethylaminoethylamino)-5H-pyrido[1,2-a]pyrimido[4,5-d]pyrimidin-5-one (Vc), mp 141-143°; ir: 1724 cm⁻¹ (CO); uv: 217 (1.74 × 10⁴), 277 (4.15 × 10⁴), 299 (2.49 × 10⁴), 352 (1.07 × 10⁴), and 365 mμ (1.05 × 10⁴).

Anal. Calcd. for C₁₆H₂₀N₆O: C, 61.52; H, 6.45; N, 26.91. Found: C, 61.59; H, 6.46; N, 26.57.

Evaporation of the combined filtrate and washings on a rotary evaporator under reduced pressure gave an oily residue. A crystalline product was deposited when the residue was allowed to sit at room temperature overnight. The solid was collected on a filter and recrystallized from ether, giving 0.35 g (20%) of N-(2-diethylaminoethyl)-2-(diethylaminoethyl)amino-4-(2-pyridinylamino)-5-pyrimidinecarboxamide, mp 121-123°; uv: 262 (2.55 × 10⁴), 275 (2.62 × 10⁴), and 293 mμ (2.58 × 10⁴).

Anal. Calcd. for C₂₂H₃₆N₈O: C, 61.65; H, 8.47; N, 26.27. Found: C, 61.41; H, 8.52; N, 26.19.

Reaction of IVa with 2-Diethylaminoethylamine.

A mixture of IVa (6.4 g) and 2-diethylaminoethylamine (35 ml) was refluxed for 20 minutes. The color of the solution changed from dark brown to dark orange. Chilling of the solution in ice caused separation of a precipitate which was collected on a filter and washed with ethanol repeatedly, giving 3.8 g (46%) of Vc, mp 141-143°. Mixture mp with Vc prepared from Va was not depressed.

2-(4-Morpholinyl)-5H-pyrido[1,2-a]pyrimido[4,5-d]pyrimidin-5-one (Vd).

A. From Va.

A mixture of Va (2.6 g) and morpholine (25 ml) was heated under reflux for 2 hours, then chilled in ice to cause separation of a precipitate which was collected on a filter, and washed with ethanol, giving 2.1 g (70%) of Vd, mp 277-279°; ir: 1724 cm⁻¹ (CO); uv: 218 (1.57 × 10⁴), 231 (1.00 × 10⁴), 287 (4.90 × 10⁴), 303 (3.3 × 10⁴), 353 (1.18 × 10⁴), and 363 mμ (1.18 × 10⁴).

Anal. Calcd. for C₁₄H₁₃N₅O₂: C, 59.35; H, 4.63; N, 24.72. Found: C, 59.23; H, 4.55; N, 24.27.

B. From IVa.

A mixture of IVa (4.0 g) and morpholine (30 ml) was heated under reflux for 1 hour, then chilled in ice. The precipitate that separated was collected on a filter, and washed with ethanol, giving 4.0 g (100%) of the product which is identical with Vd prepared by Method A, mp 278-280°.

2-(4-Methyl-1-piperazinyl)-5H-pyrido[1,2-a]pyrimido[4,5-d]pyrimidin-5-one (Ve).

A mixture of IVa (2.6 g) and 1-methylpiperazine (25 ml) was refluxed for 2.5 hours, then chilled in ice. The precipitate that separated was collected on a filter, and washed with ethanol, giving 2.6 g (83%) of Ve, mp 223-225°. Recrystallization from ethanol gave an analytical sample, mp 222-223°; ir: 1715 cm⁻¹ (CO); uv: 218 (1.57 × 10⁴), 231 (1.00 × 10⁴), 287 (4.90 × 10⁴), 303 (3.33 × 10⁴), 353 (1.18 × 10⁴), and 363 mμ (1.18 × 10⁴).

Anal. Calcd. for C₁₅H₁₆N₆O: C, 60.79; H, 5.44; N, 28.36. Found: C, 60.70; H, 5.50; N, 28.14.

2-(4-Phenyl-1-piperazinyl)-5H-pyrido[1,2-a]pyrimido[4,5-d]pyrimidin-5-one (Vf).

A mixture of IVa (2.5 g) and 1-phenylpiperazine (14 ml) was refluxed for 1 hour, then chilled. A precipitate was collected on a filter, washed with ethanol, then recrystallized from dimethylformamide, giving 2.9 g

(79%) of Vf, mp 224-226°; ir: 1715 cm⁻¹ (CO); uv: 232 (1.76 × 10⁴), 238 (1.66 × 10⁴), 289 (4.98 × 10⁴), 302 (shoulder) (3.72 × 10⁴), 355 (1.23 × 10⁴), and 3.65 mμ (1.23 × 10⁴).

Anal. Calcd. for C₂₀H₁₈N₆O: C, 67.02; H, 5.06; N, 23.45. Found: C, 67.17; H, 5.02; N, 23.29.

4-[[2-Phenyl-4-(2-pyridinylamino)-5-pyrimidinyl]carbonyl]morpholine (XIIb).

A mixture of IVb (0.5 g) and morpholine was refluxed for 1 hour, then evaporated on a rotary evaporator under reduced pressure to give an oily residue which solidified on standing. The solid material was collected on a filter, and recrystallized from ethanol, giving 0.36 g (55%) of XIIb, mp 154-155.5°; ir: 1613 cm⁻¹ (CO); uv: 273 (2.94 × 10⁴), 290 mμ (2.86 × 10⁴); nmr (DMSO-d₆): 3.68 (s, 8H, 2 CH₂CH₂), 7.06-8.62 (m, 10H), and 9.72 (s, 1H, NH).

Anal. Calcd. for C₂₀H₁₉N₅O₂: C, 66.47; H, 5.30; N, 19.38. Found: C, 66.39; H, 5.31; N, 19.16.

11-Methyl-2-(methylthio)-5-oxo-5H-pyrido[1,2-a]pyrimido[5,4-e]pyridinium Iodide (VIa).

To a hot, stirred dimethylformamide (70 ml) solution of IVa (4.8 g) was added dropwise a solution of methyl iodide (4.0 g) in dimethylformamide (20 ml). The resulting mixture was refluxed for 15 minutes, then chilled in ice. A precipitate was collected on a filter, and washed with dimethylformamide, giving 5.5 g (72%) of VIa, mp 272° dec. Recrystallization from dilute ethanol improved the mp to 275° dec; ir: 1724 cm⁻¹ (CO); uv: 216 (3.00 × 10⁴), 292 (2.13 × 10⁴), and 338 mμ (0.34 × 10⁴).

Anal. Calcd. for C₁₂H₁₁IN₄OS: C, 37.31; H, 2.87; N, 14.51. Found: C, 37.10; H, 2.84; N, 14.38.

11-Methyl-2-(methylthio)-5-oxo-5H-pyrido[1,2-a]pyrimido[4,5-d]pyrimidin-ium Iodide (VIIa).

To a clear solution obtained by heating a mixture of Va (2.0 g) and dimethylformamide (25 ml) was added methyl iodide (2.0 g). The resulting mixture was heated under gentle reflux for 20 minutes, then chilled in ice. The yellow precipitate that separated was collected on a filter and washed with water, giving 1.2 g (38%) of product, mp 268° dec. Recrystallization from water gave an analytical sample, mp 273-275°; ir: 1760 cm⁻¹ (CO); uv: 218.5 (2.06 × 10⁴), 272 (2.80 × 10⁴), and 310 mμ (1.28 × 10⁴).

Anal. Calcd. for C₁₂H₁₁IN₄OS: C, 37.31; H, 2.87; N, 14.51. Found: C, 37.55; H, 2.91; N, 14.42.

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