Synthesis of 5,6,7,8-Tetrahydro-5-oxopyrido[2,3-d]pyrimidine-6-carbonitriles and -6-carboxylic Acid Esters

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Dieckmann ring closure reactions of 4-[(2-cyanoethyl)substituted amino]-2-phenyl-5-pyrimidinecarboxylates (IIa-f) afforded several 5,6,7,8-tetrahydro-5-oxo-2-phenylpyrido[2,3-d]pyrimidine-6-carbonitriles (IIIa-f). The open-chain intermediates (IIa-f) were prepared by dechloroamination of 5-carbethoxy-4-chloro-2-phenylpyrimidine (Ia) with several 3-substituted aminopropionitriles. Alkylation of the sodium salt of 5,6,7,8-tetrahydro-8-methyl-5-oxo-2-phenylpyrido[2,3-d]pyrimidine-6-carbonitrile (IIIa) with methyl iodide in DMF resulted in methylation at C-6 to afford IV. Tosylation of IIIa in pyridine gave the corresponding tosyl ester (V) of the enolic form. Oxidative dehydrogenation at the 6,7-position resulted when IIIa reacted with thionyl chloride, affording 5,8-dihydro-8-methyl-5-oxo-2-phenylpyrido[2,3-d]pyrimidine-6-carbonitrile (VII). Dechloroamination of Ia or 5-carbethoxy-4-chloro-2-methylthiopyrimidine (Ib) with ethyl 3-ethylaminopropionate followed by Dieckmann cyclization of the resulting open-chain intermediates gave the corresponding ethyl 5,6,7,8-tetrahydro-5-oxopyrido[2,3-d]pyrimidine-6-carboxylates IX'a and IX'b, respectively. These exist predominately in the enol form and undergo alkylation and oxidation reactions similar to IIIa.

Recently, we described the preparation of several condensed pyrimidine systems generated by reactions involving 4-chloro-5-pyrimidinecarboxylates and related derivatives with several different types of bifunctional molecules (Ia-g). Further interest in the chemical diversity of these intermediates and the utility of the resulting condensed pyrimidines as potential medicinal agents prompted additional work in this area. We now report the synthesis of several novel 5,6,7,8-tetrahydro-5-oxo-pyrido[2,3-d]pyrimidine-6-carbonitriles utilizing 5-carbethoxy-4-chloro-2-phenylpyrimidine (Ia) and a number of 3-substituted amino propionitriles (2).

In a typical example, treatment of Ia with 3-methyl-aminopropionitrile in refluxing ethanol containing sodium carbonate resulted in dechloroamination, affording ethyl 4-[(2-cyanoethyl)methylamino]-2-phenyl-5-pyrimidinecarboxylate (IIa)(Scheme I). Heating IIa in refluxing ethanol with an equivalent of sodium ethoxide resulted in a Dieckmann type ring closure affording 5,6,7,8-tetrahydro-8-methyl-5-oxo-2-phenylpyrido[2,3-d]pyrimidine-6-carbonitrile (IIIa). Similarly, intermediates IIb-f (Table I) were formed by dechloroamination reactions of Ia with various 3-(substituted amino)propionitriles. Cyclization to the corresponding tetrahydropyrido[2,3-d]pyrimidines IIIb-f (Table II) proceeded smoothly in each case by the action of sodium ethoxide in refluxing ethanol.

The presence of a weak unconjugated nitrile band at 4.47 μ, an intense carbonyl band at 5.93 μ and the absence of OH absorption in the infrared spectrum of IIIa indicate that the keto form predominates over the tautomeric enol form III'a. As expected, the sodium salt showed a preponderance of the enolic form as indicated by the presence of an intense conjugated CN band at 4.62 μ and the lack of carbonyl absorption.

Alkylation of the sodium salt of IIIa with methyl iodide in DMF afforded the ketone derivative IV. It was clear that C-alkylation rather than O-alkylation had resulted, since the ir spectrum of the product showed an intense aromatic ketone band at 5.94 μ and a weak nitrile band at 4.25 μ. When IIIa was treated with tosyl chloride in pyridine, tosylation of the enol resulted, affording V. The ir spectrum showed an intense CN band at 4.55 μ and no absorption in the carbonyl region.

In a previous communication (3), we reported that 5-hydroxy-7-methyl-2-phenyl-7H-pyrrolo[2,3-d]pyrimidine-6-carbonitrile underwent a chlorination reaction with thionyl chloride to afford 6-chloro-5,6-dihydro-7-methyl-5-oxo-2-phenyl-7H-pyrrolo[2,3-d]pyrimidine-6-carbonitrile. It was of interest to determine whether a similar product would result when IIIa was allowed to react with thionyl chloride under the same conditions. An oxidation product, 5,8-dihydro-8-methyl-5-oxo-2-phenylpyrido[2,3-

Scheme I
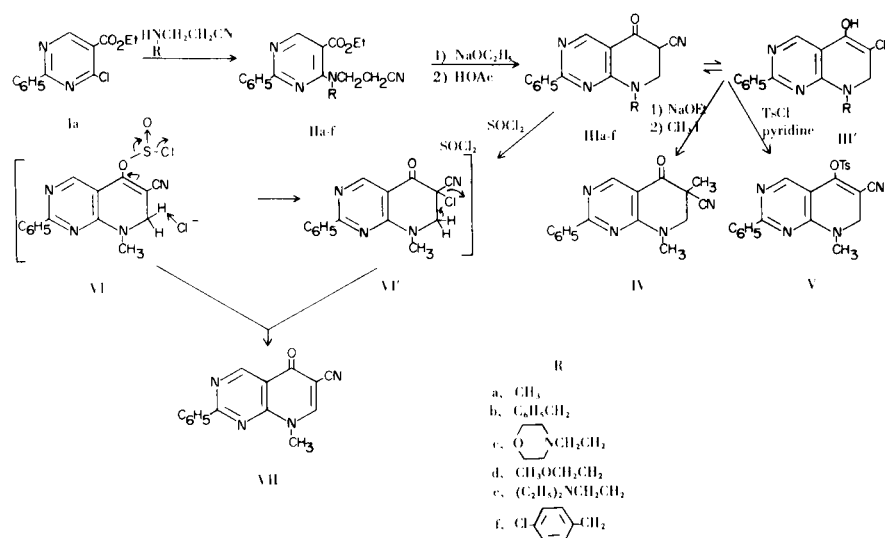
d]pyrimidine-6-carbonitrile (VII) was obtained instead. While the mechanism for the formation of VII is not certain, a labile intermediate such as sulfite VI may be involved. Elimination of sulfur monoxide and hydrogen chloride in the manner depicted would thus lead directly to the observed product. Alternatively, the chlorination product VI', possibly being generated from VI through an SNi process (3), also could produce VII by elimination of hydrogen chloride. The formation of 2-cyano-6-meth-oxy-1-naphthol from the reaction of 2-cyano-6-methoxy-

1-tetralone with thionyl chloride described by Taylor and co-workers (4) appears to be a further example of this type of reaction.
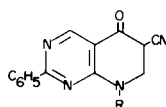
The general synthetic method described in Scheme I was extended to include the preparation of 5,6,7,8-tetra-hydro-5-oxo-pyrido[2,3-d]pyrimidine-6-carboxylic acid esters (Scheme II). Thus the dechloroamination reaction of Ia or Ib with ethyl 3-ethylaminopropionate afforded intermediates which, after Dieckmann cyclization in situ with sodium ethoxide followed by acidification, gave the

Table I

Ethyl 4-[(2-Cyanoethyl)substitutedamino]-2-phenyl-5-pyrimidinecarboxylates

Compound	R	M.p. °C	Yield, %	Recryst Solvent	Empirical Formula	Calcd. %			Found, %		
						C	H	N	C	H	N
IIa	CH₃	85-87	91	benzene-petroleum ether	C₁₇H₁₈N₄O₂	65.8	5.8	18.0	65.7	5.8	17.8
IIb	CH₂CH₂C₆H₅	67-70	87	cyclohexane	C₂₄H₂₄N₄O₂	72.0	6.0	14.0	72.2	6.0	14.2
IIc	CH₂CH₂N◯O	88-90	73	cyclohexane	C₂₂H₂₇N₅O₃	64.5	6.6	17.1	64.6	6.8	17.0
IId	CH₂CH₂OCH₃	45-47	85	petroleum ether	C₁₉H₂₂N₄O₃	64.4	6.3	15.8	64.2	6.2	15.7
IIe	CH₂CH₂N(C₂H₅)₂	42-45	76	pentane	C₂₂H₂₉N₅O₂	66.8	7.4	17.7	67.0	7.5	17.4
IIf	CH₂C₆H₄Cl	93-95	71	cyclohexane-petroleum ether	C₂₃H₂₁N₄O₂Cl	65.6	5.0	13.3	65.3	5.1	13.2

Table II

Substituted Pyrido[2,3-d]pyrimidine-6-carbonitriles

Compound	R	M.p., °C	Yield, %	Recryst. Solvent	Empirical Formula	Calcd., %			Found, %		
						C	H	N	C	H	N
IIIa	CH$_3$	218-220	88	ethanol	C$_{15}$H$_{12}$N$_4$O	68.2	4.6	21.2	68.4	4.5	21.3
IIIb	CH$_2$CH$_2$C$_6$H$_5$	199-202	87	acetone-water	C$_{22}$H$_{18}$N$_4$O	74.6	5.1	15.8	74.6	5.1	15.5
IIIc	CH$_2$CH$_2$N◯O	107-109	55	2-ethoxy ethanol-water	C$_{20}$H$_{21}$N$_5$O$_2$	66.1	5.8	19.3	66.2	5.6	19.1
IIId	CH$_2$CH$_2$OCH$_3$	172-174	73	2-ethoxy ethanol-water	C$_{17}$H$_{16}$N$_4$O$_2$	66.2	5.2	18.2	66.4	5.4	18.1
IIIe	CH$_2$CH$_2$N(C$_2$H$_5$)$_2$	205-208	83	DMF-water	C$_{20}$H$_{23}$N$_5$O	68.7	6.6	20.0	68.8	6.3	19.8
IIIf	Cl◯CH$_2$	225-227	56	ethanol	C$_{21}$H$_{15}$N$_4$OCl	67.3	4.0	15.0	67.1	3.9	14.7

corresponding pyrido[2,3-d]pyrimidines IXa (5) and IXb, respectively. Unlike their nitrile counterparts, the enol forms of these esters rather than the keto forms appear to be the predominant species in the solid state. This was made apparent by the fact that a "normal" ester carbonyl absorption was absent in the ir spectra of both IXa and IXb. A conjugated, chelated ester appeared instead for both compounds at 6.0 μ, with broad chelated OH absorption in the 3.5-4.3 μ region. Evidence for the existence of the keto form in solution was obtained from pmr spectra. For example, in the pmr spectrum of IXb the pyrimidine proton appeared as two separate resonances at 8.63 and 8.08 δ in a 1:3 ratio, the former due to the keto form and the latter to the enol form. The methyl group of the methylthio group also was found as two separate resonances at 2.47 and 2.51 δ. The OH absorption (2/3 II) was present at 11.08 δ. In example IXa the equilibrium favored the enolic form even more strongly, in an approximate ratio of 4:1. The OH resonance (4/5 II) appeared at 10.98 δ. The pyrimidine proton for the enolic form appeared at 7.43 δ, while that of the keto form was present at 7.94 δ.

Reaction of the sodium salt of IXb in DMF with methyl iodide resulted in C-alkylation, affording ethyl 8-ethyl-5,6,7,8-tetrahydro-6-methyl-2-methylthio-5-oxo-pyrido-[2,3-d]pyrimidine-6-carboxylate (X). Similarly, alkylation with ethyl iodoacetate gave ethyl 6-carbethoxy-8-ethyl-5,6,7,8-tetrahydro-2-methylthio-5-oxo-pyrido[2,3-d]pyrimidine-6-acetate (XI). Treatment of IXa with

thionyl chloride resulted in the expected oxidation giving as product the conjugated ketonic ester, ethyl 8-ethyl-5,8-dihydro-2-phenyl-5-oxo-pyrido[2,3-d]pyrimidine-6-carboxylate (XII).

Scheme II
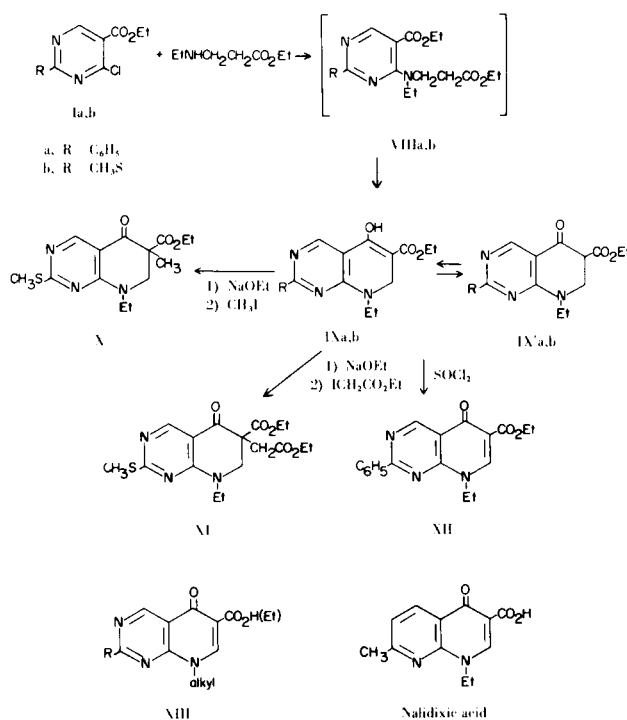
Several reports have appeared in the literature dealing with the syntheses and antibacterial properties of 5,8-dihydropyrido[2,3-d]pyrimidines of the type XIII (6), which are structural variants of the clinically effective antibacterial agent nalidixic acid (7). The common structural features present in these pyrido[2,3-d]pyrimidines is a ketonic function at the 5-position and an acidic function at the 6-position in conjugation with an alkylated pyridine nitrogen atom. In the present study, elimination of this specific conjugative effect by saturation of the 6,7-double bond constitutes a further structural departure from compounds previously reported. In examples IXa and IXb it was shown that this saturation has the further effect of bringing about a tautomeric shift from the keto form to the enol form. None of the tetrahydropyrido-[2,3-d]pyrimidines described in this initial paper showed significant in vitro antibacterial activity. Further structural modifications of the compounds described herein have been in progress and will be the subject of a subsequent communication.

EXPERIMENTAL

Melting points were determined in capillary tubes (Thomas-Hoover melting point apparatus) and are uncorrected. Infrared spectra were obtained in potassium bromide discs using a Perkin-Elmer (Model 21) spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian A-60 or a JEOL C60-HL spectrometer using dimethylsulfoxide (DMSO-d6) or deuterio-chloroform. The chemical shifts are measured in ppm (δ) with respect to tetramethylsilane. The observed spectra are in accord with assigned structures.

3-Methylaminopropionitrile was obtained from Aldrich Chemical Co., Inc. 3-(Phenethylamino)propionitrile (8), β-[2-(4-morpholinyl)ethylamino]propionitrile (9), 3-[2-(diethylaminoethyl)-amino]propionitrile (10) and 3-(p-chlorobenzylamino)propionitrile (11) and ethyl 3-ethylaminopropionate (12) were previously described.

3-(2-Methoxyethylamino)propionitrile.

To a cooled solution of 33.6 g. of 2-methoxyethylamine in 200 ml. of absolute ethanol was added dropwise 15.9 g. of acrylo-nitrile. The reaction mixture was kept below 30° during the addition. After the addition was complete the reaction mixture was kept at room temperature for 4 hours and then heated under reflux for 1 hour. The ethanol was removed on a rotary evaporator and the residual oil was distilled through a short column. The product distilling at 94-96° (0.5 mm.) amounted to 33.8 g.; ir (film): μ 4.40 (CN), 3.00 (NH).

Anal. Calcd. for $C_6H_{12}N_2O$: C, 56.2; H, 9.4; N, 21.9. Found: C, 55.8; H, 9.7; N, 22.0.

Ethyl 4-[(2-Cyanoethyl)methylamino]-2-phenyl-5-pyrimidinecar-boxylate (IIa).

A stirred mixture of 13.1 g. of 5-carbethoxy-4-chloro-2-phenylpyrimidine (Ia), 4.2 g. of 3-methylaminopropionitrile and 5.3 g. of sodium carbonate in 100 ml. of ethanol was heated under reflux for 2 hours. The reaction mixture was filtered under suction and the solvent was removed from the filtrate in a rotary evaporator. The product amounted to 14.1 g., m.p. 79-83°. The

analytical sample (m.p. 83-85°) was obtained by recrystallization from benzene-petroleum ether; ir (potassium bromide): μ 4.50 (C≡N), 5.86 (C=O).

5,6,7,8-Tetrahydro-8-methyl-5-oxo-2-phenylpyrido[2,3-d]pyrimi-dine-6-carbonitrile (IIIa).

To a solution of 0.69 g. of sodium in 150 ml. of ethanol was added 9.3 g. of IIa. The reaction mixture was heated under reflux for 1 hour and then cooled in ice. The precipitate which was deposited was collected on a filter. The sodium salt of IIIa thus formed amounted to 8.5 g., m.p. 336-344° dec.; ir (potassium bromide): μ 4.62 (intense C≡N). The salt was dissolved in 150 ml. of water and the solution was acidified with 20% acetic acid solution. The yellow precipitate which was formed amounted to 7.0 g. The analytical sample was obtained by recrystallization from ethanol; ir (potassium bromide): μ 4.47 (C≡N), 5.93 (aryl C=O).

5,6,7,8-Tetrahydro-6,8-dimethyl-5-oxo-2-phenylpyrido[2,3-d]pyri-midine-6-carbonitrile (IV).

To a solution of 2.9 g. of the sodium salt of IIIa in 50 ml. of N,N-dimethylformamide was added 1.42 g. of methyl iodide. The reaction mixture was warmed for a few minutes on a steam bath, allowed to stand at room temperature for 1 hour, and poured into 200 ml. of water. The precipitate which formed was collected on a filter and amounted to 2.0 g. Recrystallization from benzene afforded 1.2 g. of product, m.p. 203-206°; ir (potassium bromide): μ 4.25 (C≡N), 5.94 (C=O); pmr (deuterio-chloroform): δ 9.03 (s, 1, pyrimidine H), 3.74 (AB q, 2, pyridine CH_2), 3.48 (s, 3, N-CH_3), 1.6 (s, 3, C-CH_3).

Anal. Calcd. for $C_{16}H_{14}N_4O$: C, 69.0; H, 5.1; N, 20.1. Found: C, 69.1; H, 5.0; N, 19.9.

7,8-Dihydro-5-hydroxy-8-methyl-2-phenylpyrido[2,3-d]pyrimidine-6-carbonitrile p-Toluenesulfonate (V).

To a solution of 5.3 g. of IIIa in 60 ml. of dry pyridine was added 3.8 g. of tosyl chloride. The reaction mixture was warmed for a few minutes on a steam bath, whereupon a yellow precipitate was deposited. The reaction mixture was allowed to stand for 1 hour at room temperature and was then poured into 50 ml. of water. The mixture was filtered under suction, giving 7.6 g. of product. The analytical sample (m.p. 115-117°) was obtained by recrystallization from 2-ethoxyethanol; ir (potassium bromide): μ 4.55 (C≡N), 6.15 (C=C), 7.60 and 8.49 (SO_2).

Anal. Calcd. for $C_{22}H_{18}N_4O_3S$: C, 63.1; H, 4.3. Found: C, 63.1; H, 4.2.

5,8-Dihydro-8-methyl-5-oxo-2-phenylpyrido[2,3-d]pyrimidine-6-carbonitrile (VII).

A solution of 1.0 g. of IIIa in 50 ml. of boiling thionyl chloride was heated under reflux for 24 hours. The thionyl chloride was removed on a rotary evaporator, leaving a residue amounting to 1.0 g., m.p. 319-322° dec. Recrystallization from N,N-dimethyl-formamide raised the m.p. to 332-333°; ir (potassium bromide): μ 4.50 (C≡N), 6.13 (conj. aryl C=O); pmr (DMSO-d6): δ 9.54 (s, 1, pyrimidine H), 9.13 (s, 1, vinyl H), 3.98 (s, 3, NCH3).

Anal. Calcd. for $C_{15}H_{10}N_4O$: C, 68.7; H, 3.8; N, 21.4. Found: C, 68.5; H, 4.0; N, 21.5.

Ethyl 8-Ethyl-7,8-dihydro-5-hydroxy-2-phenylpyrido[2,3-d]pyri-midine-6-carboxylate (IXa).

A stirred mixture of 7.9 g. of Ia, 4.3 g. of ethyl 3-ethylamino-propionate and 3.2 g. of sodium carbonate in 100 ml. of ethanol was heated under reflux for 3 hours and subsequently filtered

under suction. The filtrate was added to a sodium ethoxide solution prepared from 0.7 g. of sodium in 100 ml. of ethanol. Within a few minutes a yellow precipitate was formed. Refluxing was continued for 1 hour and the reaction mixture was cooled in ice and filtered. The sodium salt of the product IXa thus formed was suspended in 200 ml. of water and the mixture was acidified with glacial acetic acid. The precipitate thus treated amounted to 7.5 g., m.p. 157-160°. Recrystallization from ethanol afforded 6.7 g. of product, m.p. 160-161°; ir (potassium bromide): μ 3.45-4.3 (broad OH), 5.98 (ester C=O); pmr (deuteriochloroform): δ 10.98 (s, 4/5, OH), 7.43 (s, 4/5, enol pyrimidine H), 7.94 (s, 1/5, keto pyrimidine H), 4.34 (s, 1 3/5, enol pyridine

$$CH_2),\ 4.22\ (q,\ 2,\ \overset{O}{\overset{||}{C}}\text{-}OCH_2CH_3),\ 3.62\ (q,\ 2,\ NCH_2CH_3),\ 1.29$$

$$(t,\ 3,\ \overset{O}{\overset{||}{C}}\text{-}OCH_2CH_3),\ 1.22\ (t,\ 3,\ NCH_2CH_3).$$

Anal. Calcd. for $C_{18}H_{19}N_3O_3$: C, 66.4; H, 5.9; N, 12.9. Found: C, 66.6; H, 5.6; N, 13.0.

Ethyl 8-Ethyl-7,8-dihydro-5-hydroxy-2-methylthiopyrido[2,3-d]-pyrimidine-6-carboxylate (IXb).

A stirred mixture of 11.6 g. of ethyl 4-chloro-2-methylthio-5-pyrimidinecarboxylate (Ib) 7.2 g. of ethyl 3-ethylaminopropionate and 5.3 g. of sodium carbonate in 250 ml. of ethanol was heated under reflux for 2 hours. The reaction mixture was filtered under suction into a 500 ml. flask and a solution of sodium ethoxide (1.2 g. of sodium in 100 ml. of ethanol) was added. The reaction mixture was heated with stirring under reflux for 10 minutes, during which time a yellow precipitate was formed. The reaction mixture was cooled in ice and filtered. The sodium salt of IXb thus obtained was suspended in 400 ml. of water and the mixture was acidified with glacial acetic acid. The product amounted to 11.8 g., m.p. 151-154°. The analytical sample (m.p. 155-157°) was obtained by recrystallization from ethanol (lit. ref. 5, m.p. 157°); ir (potassium bromide): μ 3.45-4.3 (broad OH), 6.0 (ester C=O); pmr (deuteriochloroform): δ 11.08 (s, 2/3 H, OH), 8.08 (s, 2/3, enol pyrimidine H), 8.63 (s, 1/3, keto pyrimidine H), 4.31 (s, 1 1/3, enol pyridine CH_2), 2.47 (s, 1/3, CH_3S), 2.51 (s, 2/3, CH_3S).

Anal. Calcd. for $C_{13}H_{17}N_3O_3S$: C, 52.9; H, 5.8; N, 14.2; S, 10.8. Found: C, 52.9; H, 5.8; N, 14.6; S, 10.7.

Ethyl 8-Ethyl-5,6,7,8-tetrahydro-6-methyl-2-methylthio-5-oxopyrido[2,3-d]pyrimidine-6-carboxylate (X).

To a solution of 6.4 g. of the sodium salt of IXb in 30 ml. of DMF was added 6.4 g. of methyl iodide. After the heat of reaction diminished, the reaction mixture was heated to 50° for a few minutes and was then allowed to stand at room temperature for 1 hour. The reaction mixture was poured into 400 ml. of water and the oily residue which was deposited crystallized on cooling and scratching. The product amounted to 4.9 g., m.p. 82-87°. Recrystallization from petroleum ether gave 4.2 g. of product, m.p. 87-89°; ir (potassium bromide): μ 5.77 (ester (ester C=O), 5.95 (ketone C=O); pmr (deuteriochloroform): δ

$$8.54\ (s,\ 1,\ pyrimidine\ H),\ 4.12\ (q,\ 2,\ \overset{O}{\overset{||}{C}}\text{-}OCH_2CH_3),\ 3.77\ (q,\ 2,$$
NCH_2CH_3), 3.63 (A, B q, 2 pyridine CH_2), 2.50 (s, 3, SCH_3)
$$1.23\ (t,\ 3,\ \overset{O}{\overset{||}{C}}\text{-}OCH_2CH_3),\ 1.14\ (t,\ 3,\ NCH_2CH_3).$$

Anal. Calcd. for $C_{14}H_{19}N_3O_3S$: C, 54.4; H, 6.2; N, 13.6; S, 10.4. Found: C, 54.1; H, 6.1; N, 13.8; S, 10.2.

Ethyl 6-Carbethoxy-8-ethyl-5,6,7,8-tetrahydro-2-methylthio-5-oxo-pyrido[2,3-d]pyrimidine-6-acetate (XI).

To a solution of 5.1 g. of the sodium salt of IXb in 50 ml. of DMF was added 6.3 g. of ethyl iodoacetate. After the initial thermal reaction had abated, the reaction mixture was heated to 50° for a few minutes and then allowed to stand at room temperature for 3 hours. The reaction mixture was poured into 400 ml. of water and the crystalline product which resulted was collected on a filter (5.5 g., m.p. 110-113°). Recrystallization from ethanol gave 4.0 g. of product, m.p. 112-114°; ir (potassium bromide): μ 5.78 (ester C=O), 5.92 (ketone C=O); pmr (deuteriochloroform): δ 8.57 (s, 1, pyrimidine), 2.50 (s, 3, SCH_3), 2.85

$$(A,\ B\ q,\ 2,\ CH_2\text{-}\overset{O}{\overset{||}{C}}\text{-}),\ 1.26,\ 1.22,\ 1.19\ (overlapping\ triplets,\ 9,$$
CH_2CH_3), 3.80 (q, 2, NCH_2CH_3).

Anal. Calcd. for $C_{17}H_{23}N_3O_5S$: C, 53.5; H, 6.1; N, 11.0; S, 8.4. Found: C, 53.7; H, 6.1; N, 11.1; S, 8.5.

Ethyl 8-Ethyl-5,8-dihydro-5-oxo-2-phenylpyrido[2,3-d]pyrimidine-6-carboxylate (XII).

A mixture of 0.5 g. of IXa in 250 ml. of thionyl chloride was heated under reflux for 5 hours. The excess thionyl chloride was removed on a rotary evaporator in vacuo. A yellow crystalline product (m.p. 187-190°) was obtained which amounted to 0.3 g. after recrystallization from ethanol; ir (potassium bromide): μ 5.88 (keto C=O), 6.00 (ester C=O); pmr (deuteriochloroform): δ 9.70 (s, 1, pyrimidine H), 8.63 (s, 1, vinyl H), 4.53 (q, 2,

$$\overset{O}{\overset{||}{C}}\text{-}OCH_2CH_3),\ 4.42\ (q,\ 2,\ NCH_2CH_3),\ 1.56\ (t,\ 3,\ \overset{O}{\overset{||}{C}}\text{-}OCH_2CH_3),$$
1.40 (t, 3, NCH_2CH_3).

Anal. Calcd. for $C_{18}H_{17}N_3O_3$: C, 66.9; H, 5.3; N, 13.0. Found: C, 66.8; H, 5.5; N, 13.0.

Acknowledgments.

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