tilled. There was obtained 3.12 g. (71.4%) of bis(*p*-tolyl)phosphinous chloride boiling at 125–128° (0.21 mm.). This value agrees on extrapolation with a previously reported[15] boiling point (345–350°).

Hydrolysis of Bis(*p*-tolyl)phosphinous Chloride.—A sample of bis(*p*-tolyl)phosphine oxide was obtained for analysis by hydrolyzing the phosphinous chloride prepared above. To 25 ml. of water was slowly added 2.66 g. (0.0107 mole) of bis(*p*-tolyl)phosphinous chloride. After stirring for 2 hr., the mixture was extracted with benzene. The benzene extract was washed with 5% sodium bicarbonate and then water, dried over magnesium sulfate, and evaporated to leave 2.30 g. (94%) of bis(*p*-tolyl)phosphine oxide, m.p. 98.5–100.5°.

Anal. Calcd. for $C_{14}H_{15}OP$: P, 13.45. Found: P, 13.41.

The infrared spectrum possessed PH (2340 cm.$^{-1}$), and P(O) (1180 cm.$^{-1}$) stretching bands.

Studies on the Tetrazole–Azidoazomethine–Tetrazole Equilibrium. III. 2-Azidopyrimidines[1]

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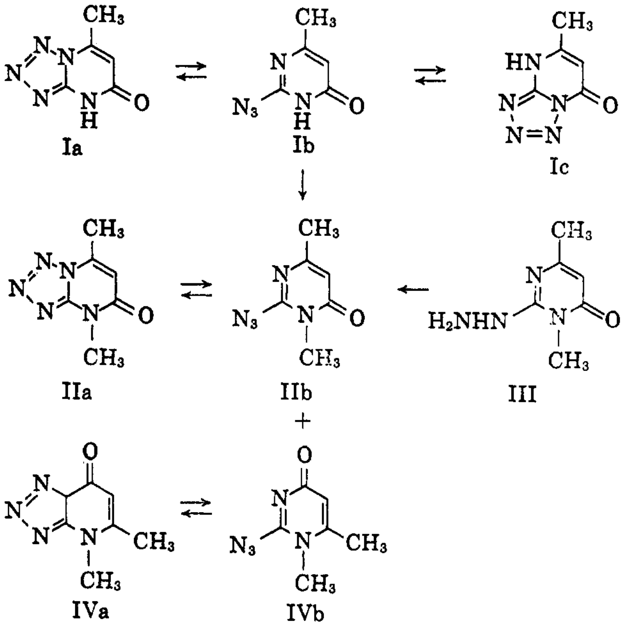
Received January 12, 1965

The rate of tautomerization as a function of temperature of 7-methyltetrazolo[1,5-*a*]pyrimidin-5(4H)-one (Ia) to 5-methyltetrazolo[1,5-*a*]pyrimidin-7(4H)-one (Ic) through 2-azido-4-methylpyrimidin-6(1H)-one (Ib) has been determined from data derived from infrared and proton magnetic resonance spectrometry. Activation parameters indicate that the rate-determining step is opening of the tetrazole ring of Ia to give the 2-azidopyrimidine intermediate Ib. The structure of I in the solid state is determined by the solvent from which it is isolated.

The azidoazomethine–tetrazole equilibrium[2] and the related isomerization of substituted 5-aminotetrazoles[3a] at elevated temperatures has been demonstrated. The existence of an equilibrium at room temperature between a bicyclic tetrazole and a tautomeric bicyclic tetrazole through an azido intermediate, however, has not been reported heretofore.[3b] This type of equilibrium is involved in solutions of I, which previously was considered by some to have the structure of 5-methyltetrazolo[1,5-*a*]pyrimidin-7(4H)-one (Ic).[4,5] We have found that I exists mainly as 7-methyltetrazolo[1,5-*a*]pyrimidin-5(4H)-one (Ia)[4] in the solid state, and mainly as a mixture of Ia and Ic in most solutions.

Although three structures (Ia, b, and c) might result from the methods[6] used to prepare I, the product was assigned structure Ic in one case[5] and apparently structure Ia in another.[7] 2-Azido-4-methylpyrimidin-6(1H)-one (Ib) was eliminated from consideration as the product by the transparency of the azido absorption region of the infrared spectrum of I in the solid state (KBr disk) and in pyridine and dimethyl sulfoxide (DMSO) solutions.[8] Both Ia and Ic were detected in the proton magnetic resonance (p.m.r.) spectra of pyridine and DMSO-d_6 solutions of I. The spectrum of I in DMSO-d_6 initially indicates the presence of only one compound; however, after about 10 min. the absorption of an additional but similar compound appears. The compound first detected, which corresponds to the structure of I in the solid state, was identified as Ia by comparison of its chemical shifts and apparent coupling constants with those of 4,7-dimethyltetrazolo[1,5-*a*]pyrimidin-5(4H)-one (IIa)[7] in DMSO-d_6 (see Table I).[9] The new compound that appears in the DMSO-d_6 solution must be Ic, which is formed from Ia through the intermediate 2-azidopyrimidine Ib. The possibility that we were observing the keto–enol equilibration of I was dismissed by infrared spectral data. Initially a solution of I in DMSO shows a band at 1690 cm.$^{-1}$ (Ia), but after 24 hr. the solution



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(1) This investigation was supported by funds from the C. F. Kettering Foundation and the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, Contract No. PH-43-64-51.

(2) C. Temple, Jr., and J. A. Montgomery, *J. Org. Chem.*, **30**, 829 (1965), and references therein.

(3) (a) R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Am. Chem. Soc.*, **77**, 2264 (1955), and prior references. (b) The existence of such an equilibrium has been considered by I. N. Goncharova and I. Ya. Postovskii [*J. Gen. Chem. USSR*, **33**, 2413 (1963)].

(4) A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," American Chemical Society, Washington, D. C., 1960.

(5) (a) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, **24**, 779 (1959); (b) C. Bulow, *Ber.*, **42**, 284 (1909).

(6) One method involved the nitrosation of 2-hydrazino-4-methylpyrimidin-6-ol[7] and another the interaction of 5-aminotetrazole either with ethyl acetoacetate or with ethyl β-aminocrotonate.[5]

(7) K. Shirakawa, Japanese Patent 777 (February 6, 1957); *Chem. Abstr.*, **52**, 4699*h* (1958).

(8) The infrared spectra of solutions were determined in an Irtran-2, fixed-thickness cell.

(9) II[7] is obtained by nitrosation of III,[10] which is prepared by hydrazinolysis of 1,6-dihydro-1,4-dimethyl-2-methylthiopyrimidin-6(1H)-one, a compound of proven structure.[11,12] Further, we have prepared 1,6-dihydro-1,4-dimethylpyrimidin-6(1H)-one[12] by oxidation of II, which proved the structure of III.

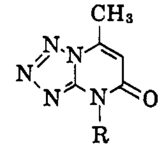
(10) C. F. H. Allen, G. A. Reynolds, J. F. Tinker, and L. A. Williams, *J. Org. Chem.*, **25**, 361 (1960).

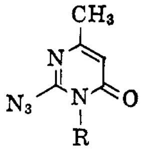
(11) H. L. Wheeler and D. F. McFarland, *Am. Chem. J.*, **42**, 106 (1909)

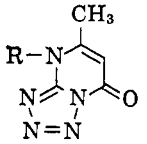
(12) F. H. S. Curd and D. N. Richardson, *J. Chem. Soc.*, 1857 (1955).

TABLE I

PROTON MAGNETIC RESONANCE SPECTRAL ASSIGNMENTS[a]







			τ value (multiplicity), J in c.p.s.[b]								
Compd.	Solvent	Concn., % (w./v.)	7–CH_3	6–H	4–CH_3	4–CH_3	5–H	1–CH_3	5–CH_3	6–H	4–CH_3
I, R = H	DMSO-d_6[c]	10	7.37 (d) (1.3)	3.72 (q)					7.60 (d) (0.8)	4.08 (q)	
	CF_3COOH	10				7.35 (d) (0.9)	3.28 (q)				
	Pyridine	<4	7.43 (d) (1.3)	3.71[d]					7.60 (d) (0.7)	4.09[d]	
II, R = CH_3	DMSO-d_6[c]	10	7.34 (d) (1.3)	3.55 (q)	6.45 (s)						
	CF_3COOH	10	7.09 (d) (1.3)	3.28 (q)	6.07 (s)	7.42 (d) (0.9)	...[e]	6.25 (s)			
	Pyridine	6.7	7.47 (d) (1.3)	3.73[d]	6.40 (s)						
	$CDCl_3$	6.7	7.23 (d) (1.3)	3.72 (q)	6.26 (s)						
IV, R = CH_3	DMSO-d_6[c]	3.5[f]							7.47 (d) (0.7)	3.89 (q)	6.14 (s)
	CF_3COOH[g]	7[f]							7.28 (d) (0.9)	3.17 (q)	6.12 (s)

[a] Spectra were obtained on a Varian A-60 spectrometer using tetramethysilane as internal reference. Probe temperature was 38°. [b] s = singlet, d = doublet, and q = quartet. Apparent values of J. [c] DMSO-d_6 = dimethyl sulfoxide-d_6. [d] Multiplicity uncertain because of solvent interference. [e] Not detected. [f] From the spectrum of a mixture of II and IV. [g] The azido tautomer was not detected.

TABLE II

RATES OF TAUTOMERIZATION OF Ia

$$\text{Ia} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Ic}$$

Temp., °K.	k_1 (= k_2), sec.$^{-1}$ $\times 10^{+5}$	Reaction, %	K_{eq} (Ic/Ia)	ΔH, kcal. mole^{-1}	ΔH^*, kcal. mole^{-1}	ΔS^*, cal. deg.$^{-1}$ mole^{-1}
311	7.70 ± 0.08	84	0.97			+2.3
319	23.0 ± 0.8	68				+2.4
326	49.3 ± 3.5	88	1.02	0	+24.8	+2.2

shows two carbonyl bands, 1690 (Ia) and 1715 (Ic) cm.$^{-1}$, of nearly the same intensity. Further, in a KBr disk the solid identified as Ia exhibits an absorption band at 1690 cm.$^{-1}$, but the solid obtained from an equilibrated solution of Ia in DMSO exhibits two carbonyl bands, one at 1690 (Ia) and another at 1710 (Ic) cm.$^{-1}$. Although the intermediate Ib was not detected in DMSO, the infrared spectrum of a trifluoroacetic acid solution[8] of I exhibits a strong azido absorption band at 2180 cm.$^{-1}$. Only one compound is detected in the p.m.r. spectrum (see Table I) of this solution, and presumably this is mainly a protonated form of Ib.

As expected, only one tautomer is detected in the p.m.r. spectrum of II in DMSO-d_6. That this tautomer is IIa instead of 2-azido-1,4-dimethylpyrimidin-6(1H)-one (IIb) is confirmed by the absence of azido absorption in the infrared spectrum of II in the solid state (KBr disk) and in a DMSO solution.[8] In contrast to I, however, both possible forms of II were detected in the p.m.r. spectrum of a trifluoroacetic acid solution. Unexpectedly, this spectrum shows that the ratio of IIa to IIb[13] is about 9:1.[14] That IIa is the major tautomer is indicated by the transparency of the infrared spectrum of this solution in the azido absorption region.[15]

In the DMSO-d_6 solution of I the concentration of Ic increases at the expense of Ia until equilibrium is obtained, which occurs in about 5 hr. at 38°. Surprisingly, the equilibrated mixture contains approximately equal amounts of Ia and Ic[16] over the range 38–53° even though the rate of conversion of Ia to Ic[18] is much faster at the higher temperature (see Table II). This result suggests that the electron density of the pyrimidine ring nitrogens of Ib are nearly the same and furthermore, that alkylation of an equilibrated mixture of Ia and Ic in DMSO with methyl iodide will give a mixture of the N-methyl derivatives II and IV. In fact, this reaction provided a mixture of two N-methyl derivatives in 56% yield, the remaining material being decomposition products. One product of the mixture was identified as II (65%) and the other tentatively as IV (35%).[19] The latter was isolated pure from the mixture and was identified as a N-methyl derivative by a carbonyl absorption band at 1730 cm.$^{-1}$ in its infrared spectrum. An unambiguous synthesis of IV was attempted by a reaction sequence similar to that used for the preparation of II.[10] Hydrazinolysis of the methyl derivative of the reported[20] 1,6-dimethyl-2-thiouracil, however, was unsuccessful.

The p.m.r. spectra show that the structure of I in the solid state is determined by the solvent from which it is obtained. Recrystallization of I from ethanol gives mainly tautomer Ia, apparently because of its lower solubility than Ic.[21] Similarly, evaporation to dryness

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(13) That protonated forms of IIa and IIb may exist in this medium is recognized.

(14) This result is attributed to the stabilization of the tetrazole form by the electron-releasing N-methyl group,[2] and to the instability of the protonated form of II.

(15) Weak azido bands may not be detected due to the cell's interference fringe pattern.[8]

(16) Although the azido group of guanyl azides preferentially forms the tetrazole ring with the nitrogen of highest electron density,[3] a value of unity for the equilibrium constant of I is consistent with the vinylogous relationship of the nitrogen atoms of the pyrimidine ring. For a discussion of this property in 2-substituted pyrimidines, see ref. 17.

(17) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, **24**, 787 (1959).

(18) I appeared to decompose in DMSO-d_6 at 100°, but the ratio of Ic to Ia was estimated to be 1.09.

(19) Alkylation of a tetrazole ring nitrogen of Ic cannot be excluded.

(20) R. N. Lacey, *J. Chem. Soc.*, 839 (1954).

(21) In isomeric compounds similar to Ia and Ic, the isomer of lower solubility results from ring closure to the pyrimidine nitrogen adjacent to the methyl group.[17]

of a trifluoroacetic acid solution of I, in which only an azido form could be detected, gives mainly Ia. In contrast, evaporation to dryness of an equilibrated solution of I in DMSO-d_6 gives a solid containing about equal amounts of Ia and Ic. Recrystallization of the last solid from ethanol, however, gives mainly Ia.

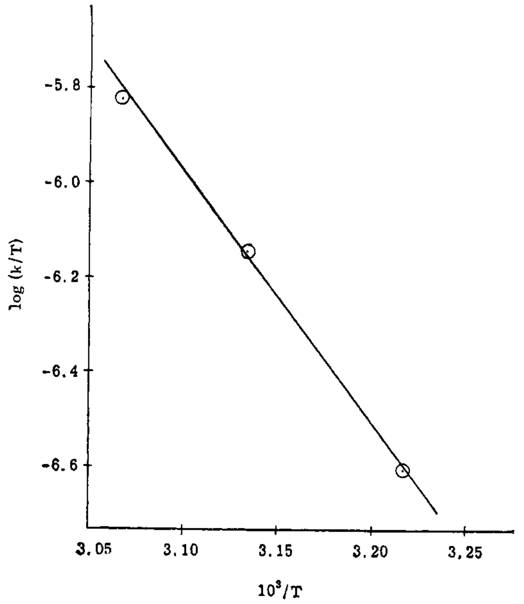

Figure 1.—Effect of temperature on the rates of tautomerization of Ia (k in sec.$^{-1}$, T in °K.).

Rates of tautomerization of I at several temperatures are recorded in Table II. The rates were first order and were observed to be linear to over 68% completion with a minimum correlation coefficient of 0.987. The sixfold increase in rate for a 15° increase in temperature did not allow us to obtain as many data at the higher temperatures, and those obtained were less reliable. This is reflected in the larger per cent variation (7%) of the rate constant at 326°K. The effect of temperature on the rate of tautomerization of I is shown in Figure 1, and the values of the activation parameters are presented in Table II. The value of the activation energy is less than that reported for the isomerization of substituted 5-aminotetrazoles, but greater than that reported for the cyclization of guanyl azides.[3] These results and the small magnitude of the entropy of activation suggest that the rate-determining step in the tautomerization is the ring opening of the tetrazolo[1,5-*a*]pyrimidine Ia (Ic) to the 2-azidopyrimidine Ib.

Although the equilibration of Ia and Ic was observed in pyridine, accurate measurement of the relative concentrations was difficult because of solvent interference and the limited solubility of I. Undoubtedly this equilibration occurs in practically all solvents in which I is soluble.

Experimental

The melting points reported were determined on a Kofler Heizbank and are corrected. The ultraviolet spectra were determined with a Cary Model 14 spectrophotometer. The infrared spectra were determined in pressed potassium bromide disks or, when indicated, in solution with a Perkin-Elmer Model 221-G spectrophotometer. The p.m.r. spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as internal reference. In the rate studies the solutions were prepared by heating I in DMSO-d_6 at the specified temperature, which was controlled by the Varian V6057 variable-temperature system. The temperature was verified by the chemical shift difference of the ethylene glycol peaks. The relative amounts of Ia and Ic were determined as a function of time from the ratio of the integrated intensities of the methyl signal from Ia and from Ic to the sum of the integrated intensities of the methyl signals. Rates were calculated using the opposed first-order reaction equation, $\ln K_{eq}(a-c) = -(k_1 + k_2)t + \text{constant}$, where K_{eq} was taken as unity and $k_1 = k_2$. In the calculation of ΔH^* the data were weighted in proportion to the number of experimental points from which each rate constant was obtained: at 311°, 25 points; at 319°, 11 points; and at 326°, 7 points.

Preparation of II.—A solution of 1,4-dimethyl-2-hydrazinopyrimidin-6(1H)-one (2.0 g.) in 1.1 *N* hydrochloric acid (12 ml.) was cooled in an ice bath and solid sodium nitrite (1.0 g.) was added with stirring. The resulting mixture was diluted with water (20 ml.) and after 1 hr. the solid was collected and dissolved in hot ethanol (75 ml.). The filtrate was chilled, and the product was collected by filtration in two crops and dried *in vacuo* over phosphorus pentoxide: yield 1.64 g. (76.5%); m.p. 180° dec. (lit.[7] m.p. 177–179°); λ_{max} in mμ ($\epsilon \times 10^{-3}$), EtOH—244 (6.30) and 261 (sh) (4.04), pH 1 and 7—244 (6.78) and 261 (sh) (4.65), and pH 13—245 (5.91) and 261 (sh) (4.42); $\bar{\nu}_{max}$ (in cm.$^{-1}$) 3080 (aromatic CH), 2945 and 2930 (aliphatic CH), 1700 (CO), 1570 and 1495 (C=C, C=N), and 1065, 1035, and 1005 (tetrazole ring).[22]

Anal. Calcd. for $C_6H_7N_5O$: C, 43.60; H, 4.24; N, 42.40. Found: C, 43.79; H, 4.17; N, 42.46.

Alkylation of I.—A solution of 7-methyltetrazolo[1,5-*a*]pyrimidin-5-ol (Ia)-5-methyltetrazolo[1,5-*a*]pyrimidin-7-ol (Ib) (1.0 g.) in dimethyl sulfoxide (10 ml.) was allowed to equilibrate at room temperature for 18 hr. To the solution was added anhydrous potassium carbonate (1.0 g.) and methyl iodide (0.5 ml.), and the whole was stirred at room temperature for 24 hr. The mixture was evaporated to dryness *in vacuo*, and the residue was washed with water (15 ml.) and recrystallized from ethanol to give 410 mg. of a mixture of two N-methyl derivatives of I, m.p. 158–159° dec. One component of the mixture was identified as II by thin layer chromatography. The second component, isolated pure below, was tentatively identified as IV by comparison of its ultraviolet spectrum with that of similar compounds,[6] and by comparison of its p.m.r. spectrum with that obtained for Ic (see Table I). The p.m.r. spectrum showed that the mixture contained 65% of IIa and 35% of IVa; λ_{max} in mμ ($\epsilon \times 10^{-3}$), pH 1—245 (5.65) and 282 (6.52), pH 7—245 (5.78) and 282 (6.56); $\bar{\nu}_{max}$ (in cm.$^{-1}$) 3080 (broad) (aromatic CH), 2955 and 2930 (aliphatic CH), 1730 and 1695 (broad) (CO), 1625, 1570, 1550, and 1500 (C=C, C=N), and 1100, 1075, 1040, 1030, and 1020 (tetrazole ring).[22]

Anal. Calcd. for $C_6H_7N_5O$: C, 43.60; H, 4.24; N, 42.40. Found: C, 43.94; H, 4.33; N, 42.71.

Extraction of the residue obtained by evaporation of the water wash with tetrahydrofuran (75 ml.) gave an additional 200 mg. of a mixture of II and IV, m.p. 151–155° dec. The total yield was 610 mg. (56%). Refrigeration of a solution of the last solid in hot tetrahydrofuran (25 ml.) deposited 40 mg. of pure IV: m.p. 219–220° dec.; λ_{max} in mμ ($\epsilon \times 10^{-3}$), EtOH—246 (4.45) and 281 (14.3), pH 1—247 (3.95) and 284 (15.5), and pH 7—247 (3.78) and 284 (15.3); $\bar{\nu}_{max}$ (in cm.$^{-1}$) 3070 (aromatic CH), 2960 and 2920 (aliphatic CH), 1730 (broad) (CO), 1625 and 1545 (C=C, C=N), and 1095, 1070, 1030, and 1020 (tetrazole ring).[22]

Anal. Calcd. for $C_6H_7N_5O$: C, 43.60; H, 4.24; N, 42.40. Found: C, 43.95; H, 4.48; N, 42.24.

The remaining material from the alkylation reaction showed only end absorption in its ultraviolet spectrum and presumably this material arose from cleavage of the pyrimidine ring under the basic conditions of the reaction.[2]

Oxidation of III.—Oxygen was bubbled for 6 hr. through a suspension of III (1.0 g.) in methoxyethanol (50 ml.) containing about 50 mg. of solid sodium hydroxide. Unreacted III (130 mg.) was removed by filtration, and the solution resulting from the addition of a solution of picric acid (1.8 g.) in methoxyethanol

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[22] E. Lieber, D. Levering, and L. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

(10 ml.) to the filtrate was evaporated to dryness *in vacuo*. The residue, a mixture of the picrates of III and 1,6-dihydro-1,4-dimethylpyrimidin-6-one, was washed with methanol, and the crude product (1.3 g.) was recrystallized from ethanol to give the analytical sample, m.p. 188–190° dec. with sublimation (lit.[12] m.p. 188–190°).

Anal. Calcd. for $C_{12}H_{11}N_5O_8$: C, 40.80; H, 3.10. Found: C, 41.04; H, 3.35.

The Synthesis of Pyrrolo[1,2-*c*]pyrimidine (6-Azapyrrocoline)[1]

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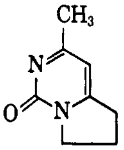
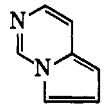
Received February 8, 1965

Pyrrolo[1,2-*c*]pyrimidine, or 6-azapyrrocoline, has been prepared by (a) cyclodehydrogenation of 3-(4-pyrimidyl)-1-propanol and (b) conversion of this propanol to the intermediate 6,7-dihydro-5H-pyrrolo[1,2-*c*]pyrimidinium *p*-toluenesulfonate followed by catalytic dehydrogenation. The intermediate propanol was synthesized from 4-methylpyrimidine *via* sodium borohydride reduction of esters of 3-(4-pyrimidyl)propenoic and 3-(4-pyrimidyl)propanoic acids. Approaches through 3-(4-pyrimidyl)-1,2-propanediol and 4-pyrimidinecarboxaldehyde were unsuccessful. The highly volatile pyrrolo[1,2-*c*]pyrimidine is similar to pyrrocoline in its ultraviolet and infrared absorption. Although its proton resonance is at low field, indicating aromaticity, it darkens rapidly at room temperature and is easily hydrogenated.

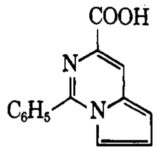
Degradation of saxitoxin, the paralytic shellfish poison, led to the isolation of 3-methyl-6,7-dihydro-5H-pyrrolo[1,2-*c*]pyrimidin-1-one (I), the structure of which was established by synthesis.[3] A literature search revealed that the corresponding parent aromatic system, pyrrolo[1,2-*c*]pyrimidine or 6-azapyrrocoline (II),[4] had never been prepared, and that only two reports of substituted pyrrolo[1,2-*c*]pyrimidines appear in the literature. One is a report[5] suggesting the 3-carboxy-1-phenyl derivative III as the structure of a product resulting from alkali treatment of the azlactone from 2-pyrrolaldehyde and hippuric acid. The second is a recent synthesis of the 3-methyl-6-phenyl derivative IV by a classical Chichibabin procedure using phenacyl bromide and 4,6-dimethylpyrimidine.[6] We now report the synthesis of the parent aromatic nucleus II.



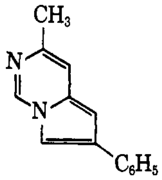
I



II



III



IV

Two general approaches were considered for the synthesis of pyrrolo[1,2-*c*]pyrimidine. One was based on the route which had been successful for the synthesis of the saxitoxin degradation product I[3] and envisaged fusion of a one-carbon unit with 2-pyrrylethylamine. However, the difficulties anticipated in ring closure to the poorly nucleophilic pyrrole nitrogen and subsequent aromatization led us to reject this approach. The other was patterned on methods which had resulted in several syntheses of pyrrocoline and involved suitably substituted 4-pyrimidines as intermediates, analogs of the substituted 2-pyridines previously used.

Our first choice of an intermediate which might be readily cyclized to pyrrolo[1,2-*c*]pyrimidine (II) was 3-(4-pyrimidyl)-1,2-propanediol (VI). This intermediate appeared readily accessible, and its use paralleled the conversion of the corresponding 3-(2-pyridyl)-[7] and 3-(2-quinolyl)-1,2-propanediols[8] to pyrrocolines. Thus 4-methylpyrimidine and diethyl oxalate gave a good yield of the α-keto ester V,[9] isolated as the potassium enolate. Reduction of V with sodium borohydride in methanol gave an oily mixture of products which contained primarily the diol VI plus some of the propanol VII. The propanol presumably arises *via* alkali-catalyzed elimination from the diol followed by reduction of the double bond.[10] Acetylation of the diol VI with acetic anhydride in pyridine gave a mixture of acetates, shown by n.m.r. analysis to be a 2:1 mixture of the diol diacetate VIII and the acetate of the propenol IX, plus a residue from which the propenol IX was obtained. The propenol most probably results from alkali-catalyzed elimination of water or acetic acid followed by hydrolysis of the propenol acetate during isolation. When acetylation was carried out with acetic anhydride–sodium acetate, the only product isolated was the propenol IX. (See Scheme I.)

With these intermediates in hand, various reactions were investigated to convert them to pyrrolo[1,2-*c*]pyrimidine (II). Pyrolysis of the mixture of acetates VIII and X at 450°, as described for the pyridine analog,[7] followed by steam distillation gave a small amount of material with a characteristic ultraviolet spectrum, later identified as that of II and containing

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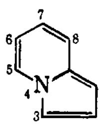
[1] Supported in part by the U. S. Army Research Office, Durham, N. C.

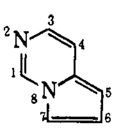
[2] Miller Research Fellow.

[3] W. Schuett and H. Rapoport, *J. Am. Chem. Soc.*, **84**, 2266 (1962).

[4] The accepted numbering systems for pyrrolo[1,2-*c*]pyrimidine and pyrrocoline are shown below. Thus the numbering system used depends on whether the compound is called a pyrrolo[1,2-*c*]pyrimidine or a 6-azapyrrocoline. We have used the former base in naming the two compounds in this series reported in the literature.[5,6]



pyrrocoline



pyrrolo[1,2-*c*]pyrimidine

[5] W. Herz, *J. Am. Chem. Soc.*, **71**, 3982 (1949).

[6] V. Boekelheide and S. S. Kertelj, *J. Org. Chem.*, **28**, 3212 (1963).

[7] V. Boekelheide and R. Windgassen, Jr., *J. Am. Chem. Soc.*, **81**, 1456 (1959).

[8] E. Roberts, M. Gates, and V. Boekelheide, *J. Org. Chem.*, **20**, 1443 (1955).

[9] W. Pfleiderer and H. Mosthaf, *Ber.*, **90**, 728 (1957).

[10] Whereas double bonds are usually stable to sodium borohydride, compare the reduction of cinnamyl alcohol to 3-phenylpropanol by lithium aluminum hydride [F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3484 (1948)] and the reduction of several α,β-unsaturated esters to the saturated alcohols by sodium borohydride.[11]

[11] M. S. Brown and H. Rapoport, *J. Org. Chem.*, **28**, 3261 (1963).