methyl proton line (6 c.p.s.) was observed in the spectrum of tetrahydro-2-methylfuran.

The absence of aldehyde or ketone in the product was indicated by a negative test obtained with 2,4-dinitrophenylhydrazine test reagent.[7]

Reaction of Maleic Anhydride with Tetrahydrothiophene.—A solution of 5.0 g. (0.003 mole) of azobisisobutyronitrile, 24.5 g. (0.25 mole) of maleic anhydride and 220 g. (2.5 moles) of tetrahydrothiophene[10] was heated at 70–73° for 5 hr. under a nitrogen atmosphere. Distillation yielded 211 g. (96%) of tetrahydrothiophene, 10 g. (41%) of maleic anhydride, 14.2 g. (31%) of 1:1 adduct, b.p. 132–168° (1 mm.), and 7.2 g. of residue.

Anal. Calcd. for $C_8H_{10}O_3S$: S, 17.2; neut. equiv., 93.1. Found: S, 16.9; neut. equiv., 94.4.

A similar experiment using benzoyl peroxide in place of azobisisobutyronitrile yielded only recovered starting materials upon distillation.

Reaction of Maleic Anhydride with Tetrahydropyran.—A solution of 49 g. (0.5 mole) of maleic anhydride and 1.21 g. (0.005 mole) of benzoyl peroxide in 430 g. (5.0 moles) of purified[5] tetrahydropyran was heated at 69–71° for 6 hr. under a nitrogen atmosphere. Distillation of the product yielded 409 g. (95%) of tetrahydropyran, 19 g. (40%) of maleic anhydride, and 51.6 g. of residue. The residue solidified to an orange glass upon cooling.

A similar reaction was carried out in which no peroxide was used, but the reaction mixture was irradiated with a General Electric sunlamp while maintained at 85–90° for 6 hr. The product was identical with that of the previous experiment.

Reaction of Maleic Anhydride wth 1,4-Dioxane.—When a solution of 39.2 g. (0.4 mole) of maleic anhydride and 352 g. (4.0 moles) of purified[11] 1,4-dioxane was maintained at 96° and illuminated by a General Electric sunlamp for 8 hr., the product was found to consist of unreacted starting materials and 12.7 g. of residue. No trace of 1:1 adduct was detected.

Reaction of 1-Octene with Tetrahydrofuran.—A solution of 56.1 g. (0.5 mole) of 1-octene, 1.21 g. (0.005 mole) of benzoyl peroxide, and 360 g. (5.0 moles) of tetrahydrofuran was held at reflux (67–68°) for 8 hr. under a nitrogen atmosphere. After 3 hr. and after 5 hr., additional 1.21-g. portions of benzoyl peroxide were added. The product was distilled through a column packed with glass helices to yield 357 g. (99%) of tetrahydrofuran, 51.3 g. (91%) of 1-octene, and 8.6 g. of residue. A solid which separated from the residue was identified as benzoic acid by its infrared spectrum and its melting point. The residue gave a negative test with 2,4-dinitrophenylhydrazine reagent.[7] A trace of aldehyde or ketone was detected both by reagent and by infrared spectrum (5.8 μ) in a small intermediate fraction boiling between tetrahydrofuran and 1-octene.

A similar experiment employing 0.82 g. (0.005 mole) of azobisisobutyronitrile in place of benzoyl peroxide yielded a 1.2 g. fraction, b.p. 79–119° (4.5 mm.), $n^{20}D$ 1.4092, which showed a weak carbonyl band at 5.85 μ in its infrared spectrum. The bulk of the product was again unreacted starting materials.

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(10) The tetrahydrothiophene was dried by distilling and discarding a small portion. It was then used without additional treatment.

(11) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 285.

Pyrimido[5,4-*e*]-*as*-triazines. II. The Preparation and Reactions of Some Heteroaromatic 5-Aminopyrimido[5,4-*e*]-*as*-triazines[1]

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Syntheses are described for the preparation of 5-amino-3-methyl- and 5-amino-3-ethylpyrimido[5,4-*e*]-*as*-triazine (VIIIa and VIIIb). These compounds are the first representatives of the pyrimido[5,4-*e*]-*as*-triazine ring system capable of resonance in both rings. Reaction of VIIIa and VIIIb with certain nucleophilic reagents under mild conditions produced other heteroaromatic pyrimido[5,4-*e*]-*as*-triazines.

In previous publications[3,4] from our laboratories we have reported the preparation of some dihydropyrimido[5,4-*e*)-*as*-triazines and the unsuccessful oxidization of 5-chloro-1,2-dihydropyrimido[5,4-*e*]-*as*-triazine (XII) to 5-chloropyrimido[5,4-*e*]-*as*-triazine (XIII).[4] Although a few other partially saturated pyrimido[5,4-*e*]-*as*-triazines have been reported,[5] a heteroaromatic representative of this ring system capable of resonance in both rings has yet to be described. This paper is concerned with the synthesis of some aromatic 5-amino- and 5-hydroxypyrimido-[5,4-*e*]-*as*-triazines and is part of our program directed toward the preparation of pteridine analogs having potential antifolic acid activity.

Treatment of ethyl *N*-(4-amino-6-chloro-5-pyrimidinyl)formimidate (IIa) with hydrazine in an attempt to prepare 5-amino-1,2-dihydropyrimido[5,4-*e*]-*as*-triazine (Va) failed to provide an identifiable product. In contrast, reaction of ethyl *N*-(4-amino-6-chloro-5-pyrimidinyl)acetimidate (IIb)[6] with a methanolic solution of hydrazine in phosphate buffer gave directly 5-amino-3-methylpyrimido[5,4-*e*]-*as*-triazine (VIIIa)[7–10] in 23% yield. Undoubtedly, in this conversion 5-amino-1,2-dihydro-3-methylpyrimido[5,4-*e*]-*as*-triazine (Vb) is an intermediate which undergoes

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(2) Affiliated with the Sloan–Kettering Institute.

(3) J. A. Montgomery and C. Temple, Jr., *J. Am. Chem. Soc.*, **82**, 4592 (1960).

(4) C. Temple, Jr., R. L. McKee, and J. A. Montgomery, *J. Org. Chem.*, **28**, 923 (1963).

(5) (a) W. Pfleiderer and K. H. Schundehutte, *Ann.*, **615**, 42 (1958); (b) G. D. Daves, Jr., R. K. Robins, and C. C. Cheng, *J. Am. Chem. Soc.*, **84**, 1724 (1961); (c) E. C. Taylor, J. W. Barton, and W. W. Paudler, *J. Org. Chem.*, **26**, 4961 (1961).

(6) J. A. Montgomery and C. Temple, Jr., *ibid.*, **26**, 395 (1960).

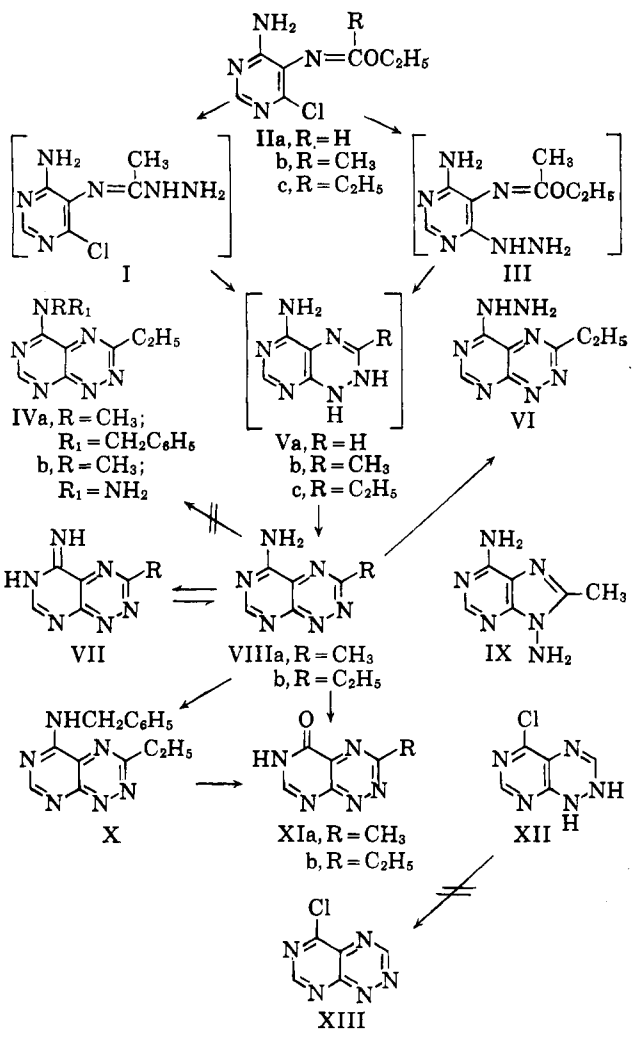
(7) The tautomerization of this compound to a structure like VII should be considered possible in view of the results obtained from studies conducted with certain 4-aminopteridines.[8] For another viewpoint see ref. 9.

(8) E. C. Taylor and C. K. Cain, *J. Am. Chem. Soc.*, **71**, 2538 (1949).

(9) A. Albert, D. J. Brown, and G. Cheeseman, *J. Chem. Soc.*, 4219 (1952).

(10) Two nonequivalent Kekulé forms for the *as*-triazine ring of pyrimido-[5,4-*e*]-*as*-triazines are possible. The Kekulé form used in this paper is reported[11] to be the more stable for *as*-triazine itself, based on quantum-mechanical computations.

(11) A. Maccoll, *J. Chem. Soc.*, 670 (1946).



spontaneous air oxidization to provide VIIIa. The intermediate preceding Vb can be either ethyl *N*-(4-amino-6-hydrazino-5-pyrimidinyl)acetimidate (III) or *N*-amino-*N'*-(4-amino-6-chloro-5-pyrimidinyl)acetamidine (I). The mild conditions required for the conversion of imidates to amidrazones,[12] however, suggests that I is the precursor to Vb. The oxidization of Vb to VIIIa but not of XII to XIII is consistent with the observation that 2,4-diamino-5,6,7,8-tetrahydro- and 2,4-diaminodihydropteridine are readily oxidized to 2,4-diaminopteridine, but that neither 5,6,7,8-tetrahydro- nor 2,4-dichloro-5,6,7,8-tetrahydropteridine is dehydrogenated under a variety of conditions.[13]

The results obtained by Naylor, *et al.*,[14] indicated that the reaction of IIb with hydrazine could give 6,9-diamino-8-methylpurine (IX). This structure and the isomeric 6-hydrazino-8-methylpurine were eliminated from consideration by the hydrogen analysis and by comparison of the ultraviolet spectrum of VIIIa with those of 6,9-diaminopurine[15] and 6-hydrazinopurine.[16]

Under conditions that converted IIb to VIIIa, ethyl *N*-(4-amino-6-chloro-5-pyrimidinyl)propionimidate (IIc)[6] and hydrazine gave a 32% yield of 5-amino-3-ethylpyrimido[5,4-*e*]-*as*-triazine (VIIIb). When this reaction was attempted in methanol in the absence of phosphate salts, the major product isolated was $C_7H_9N_7$ rather than VIIIb ($C_7H_8N_6$). The same product was obtained in 74% yield by treatment of VIIIb with hot methanolic hydrazine. Apparently the amino group of VIIIb is replaced by hydrazine to give 3-ethyl-5-hydrazinopyrimido[5,4-*e*]-*as*-triazine (VI).[17] Similar type displacements of amino groups of other bicyclic pyrimidines have been reported.[18]

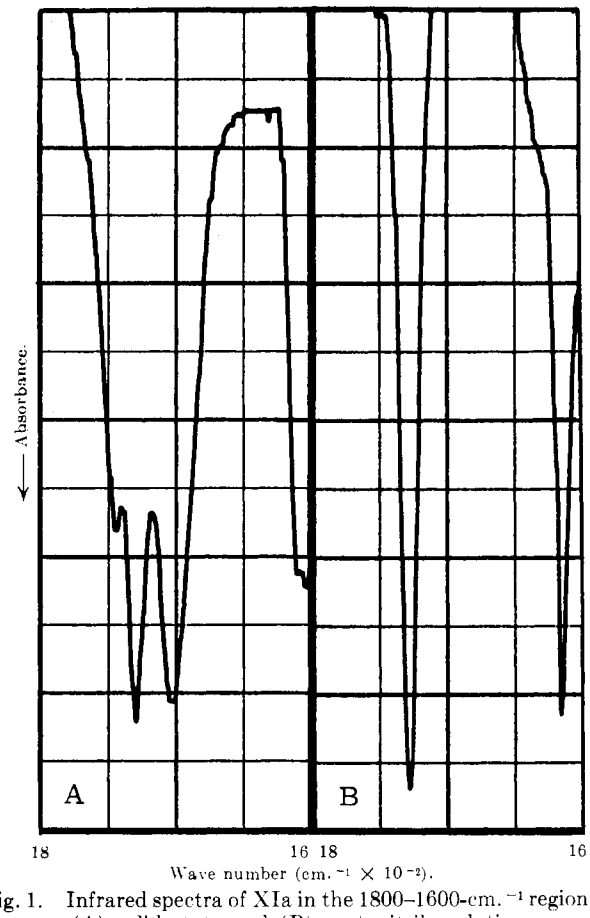


Fig. 1. Infrared spectra of XIa in the 1800–1600-cm.$^{-1}$ region for (A) solid state and (B) acetonitrile solution.

Additional support for the hydrazinolysis reaction was provided by reaction of VIIIb with benzylamine in boiling propanol to give 5-benzylamino-3-ethylpyrimido[5,4-*e*]-*as*-triazine (X) in 82% yield.[17] Contrary to expectations, amination of VIIIb with benzylmethylamine or methylhydrazine under the usual conditions was unsuccessful. Under forcing conditions (Parr bomb), these reactions gave mixtures from which neither IVa nor IVb was isolated.

The replacement of the amino group of VIIIa and VIIIb with a hydroxy group took place under remarkably mild conditions. The action of one equivalent of aqueous sodium hydroxide at room temperature converted VIIIa and VIIIb, respectively, to 3-methyl- and 3-ethylpyrimido-[5,4-*e*]-*as*-triazine-5(6*H*)-

(12) R. Roger and D. G. Neilson, *Chem. Rev.*, **61**, 200 (1961).

(13) E. C. Taylor and W. R. Sherman, *J. Am. Chem. Soc.*, **81**, 2464 (1959).

(14) R. N. Naylor, G. Shaw, D. V. Wilson, and (in part) D. N. Butler, *J. Chem. Soc.*, 4845 (1961).

(15) J. A. Montgomery and H. J. Thomas, unpublished data.

(16) J. A. Montgomery and L. B. Holum, *J. Am. Chem. Soc.*, **79**, 2185 (1957).

(17) The mechanism of this replacement reaction has not yet been determined but may involve opening of the pyrimidine ring by the basic reagent, followed by reclosure of the *as*-triazine intermediate to give the product. For similar type reactions of pteridines and purines, see ref. 18.

(18) (a) E. C. Taylor, Jr., *J. Am. Chem. Soc.*, **74**, 1651 (1952), and preceding papers; (b) C. W. Whitehead and J. J. Traverso, *ibid.*, **82**, 3971 (1960).

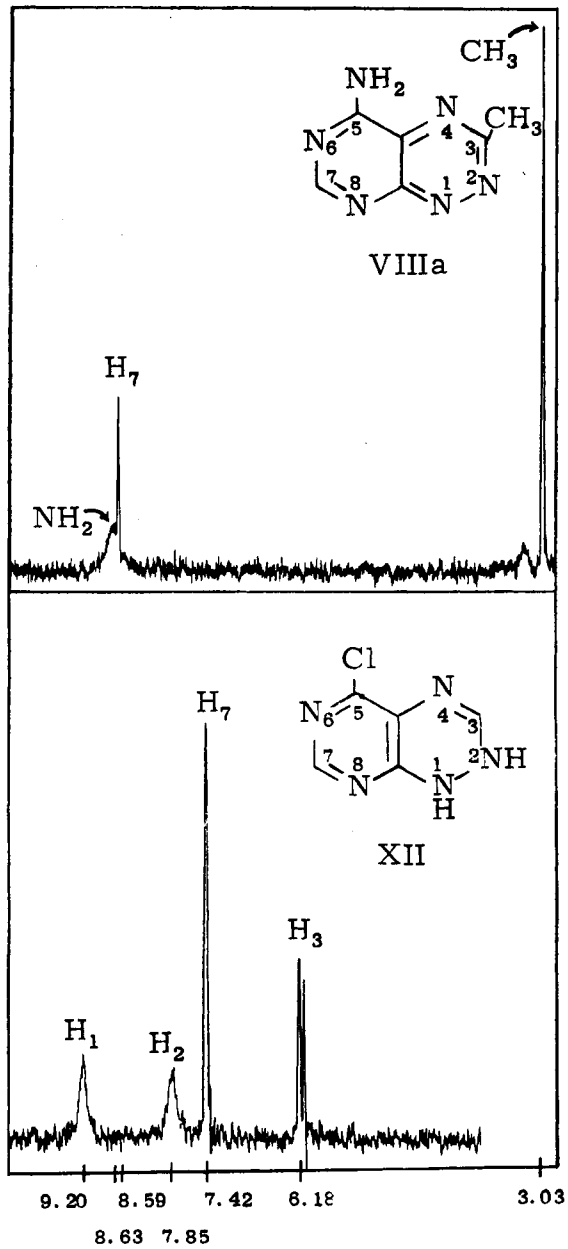


Fig. 2. Proton magnetic resonance spectra (60 Mc./sec.) of VIIIa and XII, respectively, in dimethyl sulfoxide-d_6 and dimethyl sulfoxide; field increases from left to right; chemical shifts in parts per million, relative to internal tetramethylsilane.

one (XIa and XIb) in 75 and 68% yield.[17,19] The detection of an intermediate, the structure of which is unknown, in the ultraviolet spectrum of a solution of VIIIa in 0.1 *N* sodium hydroxide implied that the conversion of VIIIa to XIa involved more than the bimolecular replacement of the amino group with the hydroxy group. The initial spectrum of this solution changed rapidly so that after about 25 minutes the maximum of the intermediate at 315 mμ had disappeared and the shoulder around 400 mμ had changed to the maximum of XIa at 372 mμ.[20] Furthermore, the ultraviolet spectrum and paper chromatograms showed that treatment of X with 0.1 *N* sodium hydroxide at room temperature caused hydrolysis of the benzylamino group to provide XIb, although the rate of conversion was slower than that of VIIIa to XIa.

(19) That other tautomers of XIa and XIb may exist is recognized.

(20) For comparison, the ultraviolet spectrum of 4-aminopteridine has been determined in 0.2 *N* sodium hydroxide.[21]

The ultraviolet spectra of XIa and 4-hydroxypteridine in an acidic medium are similar in that each shows three maxima, and dissimilar in that the long wavelength band of XIa is 26 mμ higher than the corresponding band in 4-hydroxypteridine.[21] Likewise, the long wave-length band of VIIIa occurs at a higher wave length than the corresponding band of 4-amino pteridine.[21] That the spectrum of XIa at pH 13 is practically identical with that of VIIIa at pH 7 is consistent with the observation that the spectrum of the anion of 4-hydroxypteridine closely resembles the spectrum of the neutral molecule of 4-aminopteridine.[21] In addition, replacement of the amino group of 4-aminopteridine with an alkylamino group produced a shift in the maxima to longer wave lengths,[9] and the same effect is observed by replacement of the amino group of VIIIb with a benzylamino group to give X.

The infrared spectrum of XIa in the solid state is unusual, not only in that it exhibits three carbonyl bands,[22] but that the bands occur at higher wave numbers than would be anticipated (Fig. 1). A solution of XIa in acetonitrile shows only one band in the carbonyl region (Fig. 1) and this suggests that the multiple bands in the solid state spectrum are due to crystal-orientation effects. No doubt the high frequency of this carbonyl absorption is associated with the electron-withdrawing effect of the triazine ring.

Comparison of the p.m.r. spectrum of XII with that of VIIIa at 60 Mc./sec. showed the expected differences (Fig. 2).[23] The spectrum of XII showed not only the C-3 and C-7 protons, but also the N-1 and N-2 protons, exchangeable with deuterium oxide. The doublet at 6.18 p.p.m., with a coupling constant of 3.0 c.p.s., is attributed to the spin–spin interaction of the proton at C-3 with the proton at N-2. The spectrum of VIIIa consisted of three bands with relative intensities 3:1:2, which are assigned to the 3-CH_3, the 7-ring proton, and the 5-NH_2, respectively.

Experimental

The melting points reported were determined on a Kofler Heizbank and are corrected. The ultraviolet and infrared spectra, respectively, were determined in aqueous solution with a Cary Model 14 recording spectrophotometer and in pressed potassium bromide disks with a Perkin-Elmer, Model 221, spectrophotometer.

Ethyl N-(4-amino-6-chloro-5-pyrimidinyl)formimidate (IIa).—A suspension of 6-chloro-4,5-diaminopyrimidine (1.27 g., 8.77 mmoles) in ethyl orthoformate (50 ml.) was heated with vigorous stirring at 83° (preheated oil bath) for 30 min., and then the temperature was raised to 95° within 10 min. After filtration the solution was evaporated to dryness, and the residue was washed with petroleum ether (85–105°) and dried *in vacuo* over phosphorus pentoxide; yield, 1.20 g. (68%); m.p. 109–110°. Recrystallization of this sample from benzene–petroleum ether (85–105°) did not raise the melting point. λ_{max} mμ ($\epsilon \times 10^{-3}$) at pH 7: 250 (7.26), 282 (6.74). $\bar{\nu}_{max}$ cm.$^{-1}$: 3450 and 3280 (NH); 2980 and 2900 (aliphatic CH); 1640, 1630, and 1550 (NH, C=C, C=N).

Anal. Calcd. for $C_7H_9ClN_4O$: C, 41.85; H, 4.48; Cl, 17.70; N, 27.90. Found: C, 42.14; H, 4.76; Cl, 17.8; N, 28.23.

3-Ethyl-5-hydrazinopyrimido[5,4-*e*]-*as*-triazine (VI).—A suspension of 5-amino-3-ethylpyrimido[5,4-*e*]*as*-triazine (250 mg.,

(21) A. Albert, D. J. Brown, and G. Cheeseman, *J. Chem. Soc.*, 474 (1951).

(22) D. J. Brown and S. F. Mason [*J. Chem. Soc.*, 3447 (1956)] reported that the infrared spectrum of 4-hydroxypteridine in the solid state showed two carbonyl bands.

(23) The p.m.r. spectra were determined with a Varian Associates Model A-60 spectrometer. Probe temperature was 42 ± 1°.

1.42 mmoles) in methanol (5 ml.) containing anhydrous 95% hydrazine (0.05 ml.) was refluxed for 4 hr., and the mixture was allowed to stand at room temperature overnight. The pure solid was collected by filtration, washed with methanol (4 ml.), and dried *in vacuo* over phosphorus pentoxide; yield, 200 mg. (74%). This compound decomposed rapidly without melting above 200°. The sample was recrystallized from N,N-dimethylformamide–ethanol. λ_{max} mμ ($\epsilon \times 10^{-3}$) at pH 1: 270 (4.44), 372 (7.35). $\bar{\nu}_{max}$ cm.$^{-1}$: 3400 and 3260 (NH); 3080 (aromatic CH); 2980, 2945, 2860, and 2820 (aliphatic CH); 1625 (NH); 1555 and 1485 (C=C, C=N).

Anal. Calcd. for $C_7H_9N_7$: C, 43.95; H, 4.72; N, 51.25. Found: C, 43.90; H, 4.92; N, 51.32.

From the combined filtrate and wash, 50 mg. of VIIIb slightly contaminated with VI, was recovered.

5-Amino-3-methylpyrimido[5,4-*e*]-*as*-triazine (VIIIa).—Solid ethyl *N*-(4-amino-6-chloro-5-pyrimidinyl)acetimidate (2.0 g., 9.3 mmoles)[6] was added to a solution of sodium dihydrogen phosphate hydrate (1.35 g.) and disodium hydrogen phosphate (1.35 g.) in methanol (10 ml.) and water (25 ml.) containing 95% hydrazine (0.42 ml.). The mixture was heated at 80° for 2 hr. and the resulting solution was allowed to stand at room temperature overnight. The dark crystals that deposited were collected by filtration, washed with water (5 ml.), and dried *in vacuo* over phosphorus pentoxide; yield, 500 mg. This solid was recrystallized from ethanol (50 ml.) to yield 350 mg. (23%) of product in two crops, m.p. 277–280° dec. λ_{max} mμ ($\epsilon \times 10^{-3}$) at pH 1: 245 (8.25), 350 (8.40), 358 (sh) (8.25); at pH 7: 252 (13.6), 280 (sh) (2.56), 372 (5.88). $\bar{\nu}_{max}$ cm.$^{-1}$: 3290 and 3100 (broad) (NH); 1655 (NH); 1575 and 1510 (C=C, C=N); 1445, 1350, and 1220 (strong unassigned bands).

Anal. Calcd. for $C_6H_6N_6$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.18; H, 3.95; N, 51.90.

5-Amino-3-ethylpyrimido[5,4-*e*]-*as*-triazine (VIIIb) was prepared by a similar process from 2.0 g. of ethyl *N*-(4-amino-6-chloro-5-pyrimidinyl)propionimidate[6]; yield, 500 mg. (32%); m.p. 223–225° dec. λ_{max} mμ ($\epsilon \times 10^{-3}$) at pH 1: 246 (8.34), 350 (8.34), 359 (sh) (8.17); at pH 7: 253 (13.65), 371 (5.90). $\bar{\nu}_{max}$ cm.$^{-1}$: 3290 and 3100 (NH); 2975, 2940, and 2880 (aliphatic CH); 1650 (NH); 1570 and 1510 (C=C, C=N).

Anal. Calcd. for $C_7H_8N_6$: C, 47.72; H, 4.55; N, 47.72. Found: C, 47.60; H, 4.61; N, 47.98.

5-Benzylamino-3-ethylpyrimido[5,4-*e*]-*as*-triazine (X).—A solution of 5-amino-3-ethylpyrimido[5,4-*e*]-*as*-triazine (1.0 g., 5.7 mmoles) in propanol (20 ml.) containing benzylamine (3.0 ml.) was refluxed for 5 hr. and evaporated to a small volume *in vacuo*. After this residue was washed on a funnel with water (60 ml.) to remove an insoluble dark oil, the remaining solid was dried *in vacuo* over phosphorus pentoxide to yield 1.28 g. (82%), m.p. 143–145° dec. For analysis a sample was recrystallized from petroleum ether (85–105°); m.p. 153–154° dec. λ_{max} mμ ($\epsilon \times 10^{-3}$) at pH 1: 223 (15.6), 254 (5.85), 362 (sh) (12.1), 369 (12.3); at pH 7: 224 (17.9), 257 (9.75), 385 (8.35). $\bar{\nu}_{max}$ cm.$^{-1}$: 3190 (NH); 2950 and 2910 (aliphatic CH); 1600, 1585 (sh), 1560, and 1500 (C=C, C=N).

Anal. Calcd. for $C_{14}H_{14}N_6$: C, 63.18; H, 5.27; N, 31.55. Found: C, 63.22; H, 5.21; N, 31.68.

3-Methylpyrimido[5,4-*e*]-*as*-triazin-5(6H)-one (XIa).—A suspension of 5-amino-3-methylpyrimido[5,4-*e*]-*as*-triazine (250 mg., 1.54 mmoles) in 1.07 *N* sodium hydroxide (1.65 ml.) was stirred at room temperature for 3 hr. The resulting solution was neutralized with 1.03 *N* hydrochloric acid (1.71 ml.) and evaporated to dryness *in vacuo*. This residue was extracted with two 25-ml. portions of acetone, and the combined extracts were evaporated to yield 190 mg. (75%). Recrystallization of this solid from tetrahydrofuran–petroleum ether (85–105°) gave the analytical sample; m.p. 199–200° solidifies and remelts at 213–215 dec. λ_{max} mμ ($\epsilon \times 10^{-3}$) at pH 1: 236 (8.7), 264 (5.36), 336 (5.28). At pH 7: 249 (12.4), 355 (3.73); at pH 13 : 251 (15.7), 278 (sh) (2.96), 372 (4.66). $\bar{\nu}_{max}$ cm.$^{-1}$: 3200 (NH); 2900–2500 (acidic H); 1750, 1735, and 1710 (C=O); 1610, 1595, 1540, and 1520 (C=C, C=N).

Anal. Calcd. for $C_6H_5N_5O$: C, 44.20; H, 3.07; N, 42.90. Found: C, 44.30; H, 3.03; N, 42.79.

3-Ethylpyrimido[5,4-*e*]-*as*-triazin-5(6H)-one (XIb) was prepared by a similar process from 500 mg. of 5-amino-3-ethylpyrimido[5,4-*e*]-*as*-triazine: yield, 340 mg. (68%) m.p. 183–185° dec. A second recrystallization from tetrahydrofuran–petroleum ether gave the analytical sample; m.p., 185–188° dec. λ_{max} mμ ($\epsilon \times 10^{-3}$) at pH 1: 237 (8.70), 265 (5.65), 338 (6.05); at pH 7: 250 (12.7), 360 (3.80); at pH 13: 250 (12.2), 280 (sh) (3.4), 373 (4.68). $\bar{\nu}_{max}$ cm.$^{-1}$: 3200 and 3150 (NH); 2980 (aliphatic CH); 2900–2500 (acidic H); 1730 and 1700 (C=O); 1610 (sh), 1600, 1540, and 1520 (C=C, C=N).

Anal. Calcd. for $C_7H_7N_5O$: C, 47.40; H, 3.95; N, 39.50. Found: C, 47.00; H, 3.78; N, 39.39.

Acknowledgment.—The authors are indebted to Dr. W. J. Barrett and the members of the Analytical Section of Southern Research Institute who performed the spectral and most of the analytical determinations reported, and to Dr. W. C. Coburn and Mrs. M. C. Thorpe for their helpful discussion of the infrared and proton magnetic spectra. Some of the analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Aromaticity in Heterocyclic Systems. I. The Synthesis and Structure of Certain 4,6-Dihydroxyimidazo[4,5-*c*]pyridines[1]

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The synthesis of the imidazo[4,5-*c*]pyridine ring has been accomplished for the first time from imidazole intermediates. 4,6-Dihydroxyimidazo[4,5-*c*]pyridine and related 2-substituted derivatives have been prepared for the first time from the requisite 4-imidazoleacetamide-5-carboxylic acid ester. 4,6-Dihydroxyimidazo[4,5-*c*]-pyridine (I) has been shown by n.m.r. to exist as the diketo form Ia. This accounts for the ease of pyridine ring cleavage of the 4,6-dihydroxy compounds in the presence of hot acid or base. Evidence is considered which supports the existence of the more aromatic enol form Ic present as the anion in dilute base.

Although the synthesis of 4-aminoimidazo[4,5-*c*]-pyridine (3-deazaadenine) and 4-hydroxyimidazo[4,5-*c*]pyridine (3-deazahypoxanthine) previously has been reported,[3] other purine analogs such as 4,6-dihydroxyimidazo[4,5-*c*]pyridine (I), the xanthine analog, and 2,4,6-trihydroxyimidazo[4,5-*c*]pyridine (II), the analog of uric acid, have not been recorded previously. Pre-

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(2) In part from the Master's theses of Claude V. Greco and Calvin G. Beames, Jr., New Mexico Highlands University, 1953 and 1955.

(3) C. A. Salemink and G. M. Van der Want, *Rec. trav. chim.*, **68**, 1013 (1949).