benzene in 40% yield from benzenediazonium tetrafluoroborate was effected by adding cuprous chloride to the reaction mixture.

Product Analyses.—After complete addition of $NO^+BF_4^-$ or $NO^+SbF_6^-$ to the imine in acetonitrile a measured amount of a standard, usually nitromethane, was added to the reaction solution and an aliquot was removed for pmr analysis. Analyses were usually performed within 1 hr after initiation of reaction, although no change in product composition was observed over longer periods of time. A pmr spectrum was taken and integrated within 10 min after the sample was placed in the probe at 41° so as to minimize decomposition of diazonium salt. For spectra taken within 10 min no noticeable decomposition was observed. Another spectrum was recorded after 20 min in the nmr probe; only when the unsubstituted benzenediazonium ion was produced was there a noticeable change in the spectrum. Products were identified by spectral comparison to the authentic materials under comparable conditions. Yields were determined by averaging several integrations of the absorption signals for products. Reproducibility was ±2% when averaged over several reactions of the same components. Comparison was made both to the added standard and to the total phenyl region with no noticeable difference. Except for III and IV, absorptions for both the carbonyl compound and benzenediazonium ion were clearly distinguishable by pmr spectroscopy. Product per cent yields determined by this method follow: IIa, 95; IIb, 95; IIc, 95; IId, 90; IIe, 83; IIf, 90; IIg, 95; IIh, 90; IIi, 83; IIj, 75. Products from the reaction of III with $NO^+BF_4^-$ were detected by glpc and ir analyses. Benzil was recovered in good yield after treatment of IV with $NO^+BF_4^-$ in acetonitrile and work-up in dichloromethane under conditions where both monoanil and dianil could have been detected.

Registry No.—Nitrosonium ion, 33904-18-6.

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The Novel Reaction of 1,3-Dimethyl-6-amino-5-nitrosouracil with Lead Tetraacetate[1]

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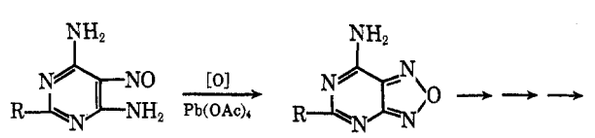
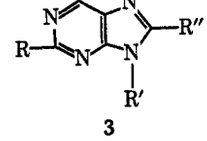
Lead tetraacetate oxidation of 1,3-dimethyl-6-amino-5-nitrosouracil (**4**) in glacial acetic acid solution results in rapid discharge of the purple color of **4**, evolution of nitrogen, and the formation of 1,3,6,8-tetramethyl-2,4,5,7-(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-oxide (**6**), along with a minor amount of 4,6-dimethyl-5,7-(4*H*,6*H*)-furazano[3,4-*d*]pyrimidinedione (**5**). The structure of **6** was established by reductive and hydrolytic studies.

We have described in a recent paper[4] the lead tetraacetate oxidation of a series of 4,6-diamino-5-nitrosopyrimidines (**1**) to 7-aminofurazano[3,4-*d*]pyrimidines (**2**), and the subsequent utilization of the latter as versatile intermediates for the unequivocal synthesis of 9-substituted adenines (**3**). The present paper describes the novel and unexpected result of lead tetraacetate oxidation, under identical conditions, of 1,3-dimethyl-6-amino-5-nitrosouracil (**4**).



1 **2**



3

Addition of lead tetraacetate to an acetic acid solution of **4** at room temperature resulted in nitrogen evolution, rapid discharge of the purple color of **4**, and the separation of a yellow, crystalline solid, mp 360–362° dec. Evaporation of the filtrate and recrystallization of the residue gave the expected[4] product, 4,6-dimethyl-5,7(4*H*,6*H*)-furazano[3,4-*d*]pyrimidinedione (**5**), in low (19%) yield. Microanalytical and mass spectral data on the yellow solid, mp 360–362° dec, established the molecular formula $C_{12}H_{12}N_6O_5$, while a strong M − 16 peak in the mass spectrum indicated the presence of a labile oxygen, most probably an *N*-oxide.[5] This conclusion was confirmed by chemical reduction with sodium dithionite at room temperature to give a pale yellow solid, mp 385°, which was shown to be 1,3,6,8-tetramethyl-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone (**8**) by comparison with an authentic sample fortuitously available in our own laboratory.[6] Thus the lead tetraacetate oxidation product of **4** must be one of the two possible *N*-oxides **6** or **7** of **8**. That the major oxidation product of **4** was the 10-oxide (**6**) and not the 9-oxide (**7**) was demonstrated unequivocally by hydrolytic and other degradative reactions which are summarized below.

Although dilute alkaline hydrolysis of **8** is known to give 3,5-bis(methylamino)-*N*,*N*′-dimethylpyrazine-2,6-dicarboxamide (**9**) in excellent yield,[6] analogous hydrolysis of **6** yielded three products, 3,5-bis(methylamino)-*N*,*N*′-dimethylpyrazine-2,6-dicarboxamide 1-oxide (**10**), 3,5-bis(methylamino)-6-carboxy-*N*-methylpyrazine-2-carboxamide 1-oxide (**11**), and 1,3-dimethyl-5-methylaminocarbonyl-6-methylamino-1*H*-imidazo[4,5-*b*]pyrazin-2(3*H*)-one (**12**) in yields of 20, 20, and 50%, respectively. Compound **10** was readily deoxygenated to the known **9** with triethyl phosphite. Re-

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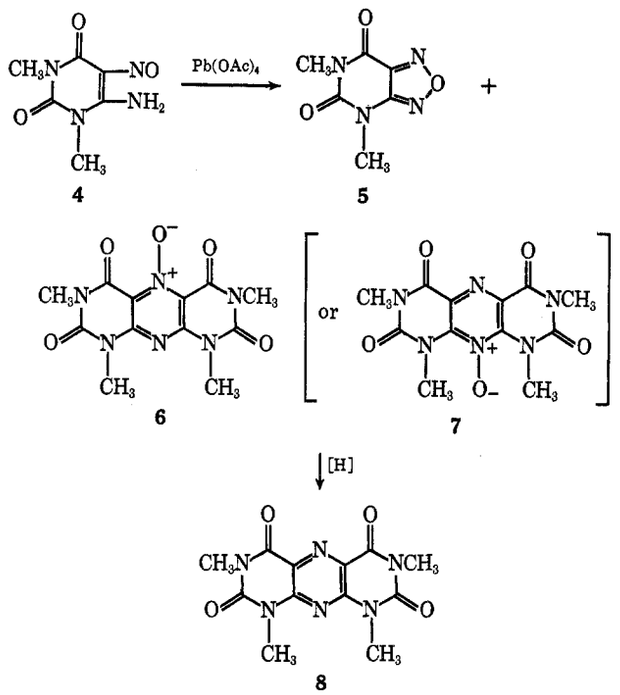
(3) School of Chemical Sciences, University of East Anglia, Norwich, England.

(4) E. C. Taylor, G. P. Beardsley, and Y. Maki, *J. Org. Chem.*, **36**, 3211 (1971).

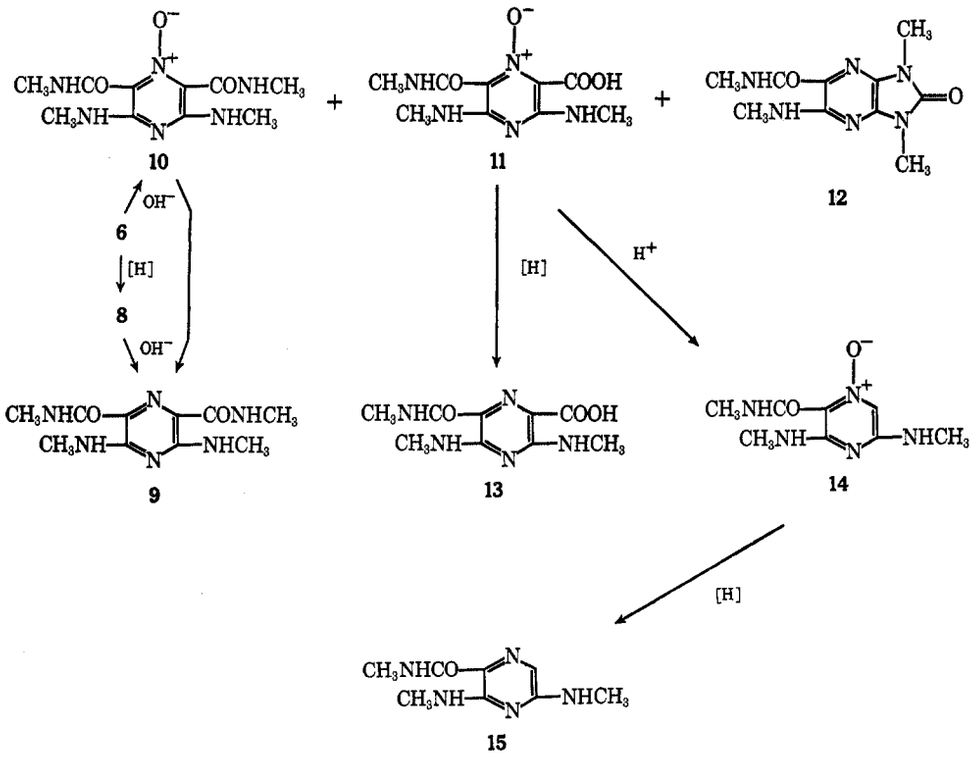
(5) T. A. Bryce and J. R. Maxwell, *Chem. Commun.*, 206 (1965).

(6) E. C. Taylor, C. K. Cain, and H. M. Loux, *J. Amer. Chem. Soc.*, **76**, 1874 (1954). The melting point of **8** was reported to be 403–404°, but a redetermination using a corrected thermometer showed it to be 385°.



duction of **11** with sodium dithionite gave 3,5-bis(methylamino)-6-carboxy-*N*-methylpyrazine-2-carboxamide (**13**), while treatment of **11** with trifluoroacetic acid at room temperature resulted in rapid decarboxylation to give 3,5-bis(methylamino)-*N*-methylpyrazine-2-carboxamide 1-oxide (**14**). Reduction of the latter compound with sodium dithionite gave 3,5-bis(methylamino)-*N*-methylpyrazine-2-carboxamide (**15**).

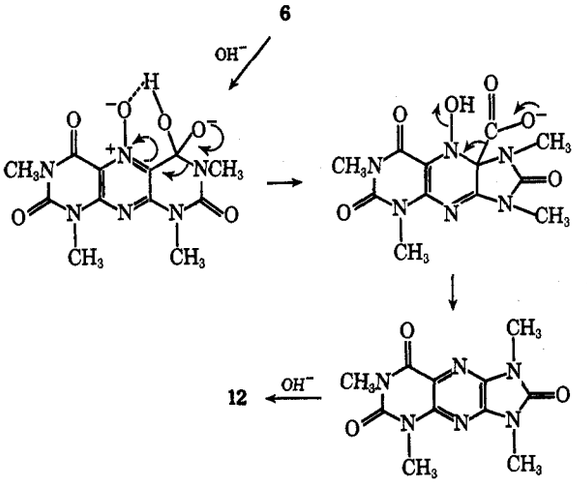
The position of the *N*-oxide function in the above pyrazine degradation products of **6** (and, as a consequence, the establishment of the position of the *N*-oxide grouping in **6** itself) was deduced from the following observations. (a) There is a marked difference between the position of the carboxylic acid C=O stretching bands of **11** and **13** (1695 and 1725 cm^{-1}, respectively), which is explicable only in terms of the effect of the *N*-oxide grouping on the ortho-situated carboxyl grouping, and would not be expected if the *N*-oxide grouping were on N_4 rather than N_1. (b) The nmr spectrum of **14** shows the C_6 H at δ 6.99, whereas the C_6 H in the deoxygenated pyrazine **15** appears at δ 7.06. The slight upfield shift of the ring proton in **14** is consistent with previous observations[7] on the effect of an *N*-oxide grouping on the chemical shift of α-ring protons. (c) Although **11** underwent smooth decarboxylation upon treatment with trifluoroacetic acid at room temperature, the corresponding deoxygenated pyrazine **13** was stable under the same conditions. This is again in accord with placement of the *N*-oxide grouping on the ring nitrogen adjacent to the carboxyl grouping.[8] (d) The formation of **12** is consistent only with the *N*-10-oxide structure **6** and cannot be explained satisfactorily on the basis of the alternate 9-oxide structure **7**. The structure of **12**, $C_{10}H_{14}N_6O_2$, was derived on the basis of combustion analysis and ir, nmr, and mass spectral data. Thus, **12** exhibited ir bands at 3390, 3310, 1695, and 1650 cm^{-1}, indicating clearly that both pyrimidine rings in the parent compound **6** had suffered cleavage by the action of alkali. The nmr spectrum of **12** showed that all four *N*-methyl groupings were still present (δ 3.30, 3.14, 3.00, and 2.86 in trifluoroacetic acid), although these chemical shifts were all different from those exhibited by the *N*-methyl groups in **6**. Compound **12** could be converted into a monoacetate with acetic anhydride which still, however, showed an NH band in its ir spectrum (3325 cm^{-1}). The absence of an *N*-oxide grouping in **12**,



(7) For leading references, see A. R. Katritzky and J. M. Logowski, "Chemistry of the Heterocyclic N-Oxides," Academic Press, New York, N. Y., 1971, p 16.

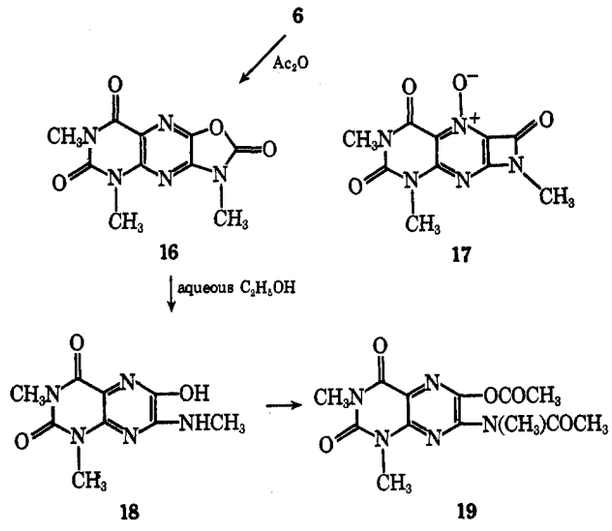
(8) See ref 7, pp 382–383.

indicated by the absence of an M − 16 peak in its mass spectrum, was confirmed by its stability to Raney nickel and to sodium dithionite. We suggest that **12** is formed from **6** by the mechanism outlined below, in which the ring contraction step is a benzylic acid type rearrangement similar to that firmly established for the conversion of alloxan to alloxanic acid.[9] The unique feature of the rearrangement in the present case is that concerted decarboxylation and dehydration lead to aromatization of the pyrazine ring. The transformation of **6** to **12** is possible only if the *N*-oxide grouping is placed on N-10.



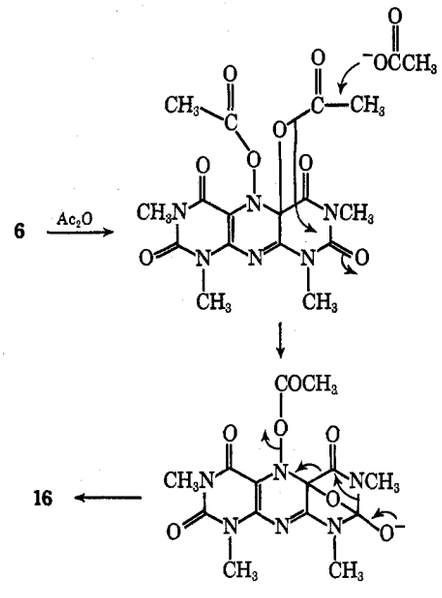
Further evidence in support of **6** (as opposed to **7**) for the lead tetraacetate oxidation product of **4** was obtained upon treatment of **6** with acetic anhydride. One of the two products formed was the deoxygenated pyrimidopteridine **8**; there is precedent for this deoxygenation in the conversion of phenazine *N*-oxide to phenazine with acetic anhydride.[10] The other product, mp 248°, was shown by microanalytical and mass spectral data (*m/e* 263) to have the molecular formula $C_{10}H_9N_5O_4$. This compound was not an *N*-oxide, as evidenced by the absence of an M − 16 peak. Its ir spectrum showed three carbonyl bands at 1825, 1720, and 1675 cm^{-1}; its nmr spectrum showed only three methyl groups at δ 3.7, 3.55, and 3.5. These three methyl groups account for all of the protons in the molecule.

These data suggest that this product contains two rings in addition to a pyrazine ring; one is apparently an unchanged fused 1,3-dimethyluracil and the other must result from the loss of methyl isocyanate from **6**. We suggest that this compound possesses structure **16**; although the high frequency carbonyl band at 1825 cm^{-1} might be explicable in terms of the *N*-methylazetinone structure (**17**),[11] such a formulation is inconsistent with mechanistic considerations (*vide infra*), with the absence of an M − 16 peak in its mass spectrum, and with its conversion with hot aqueous alcohol to 1,3-dimethyl-6-hydroxy-7-methylaminolumazine (**18**). Treatment of this latter compound with acetic anhydride gave the diacetate **19**, whose structure was confirmed by microanalysis, its ir spectrum (which revealed the lactim *O*-acetate grouping at



1775 cm^{-1}),[12] and its nmr spectrum (see Experimental Section).

We suggest that **16** is formed from **6** as depicted below. It should be noted that this interpretation requires that the *N*-oxide grouping on **6** be positioned at N-10; no reasonable mechanism leading to **16** from **7** could be envisaged.



It should be noted that **5** is apparently *not* an intermediate in the formation of **6** (from **4**). Thus, oxidation of 1,3-di(*n*-butyl)-6-amino-5-nitrosouracil (**20**) with lead tetraacetate in glacial acetic acid gave 1,3,6,8-tetra(*n*-butyl)-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-oxide (**21**). Oxidation of a mixture of 1,3-dimethyl- and 1,3-di(*n*-butyl)-6-amino-5-nitrosouracils (**4** and **20**, respectively) gave, as major products, a mixture of **6**, **21**, and the crossed product, 1,3-dimethyl-6,8-di(*n*-butyl)-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-oxide (**22**). On the other hand, oxidation of a mixture of **5** and **20** gave only the tetra(*n*-butyl) oxide **21**; **5** was recovered unchanged in 90% yield.

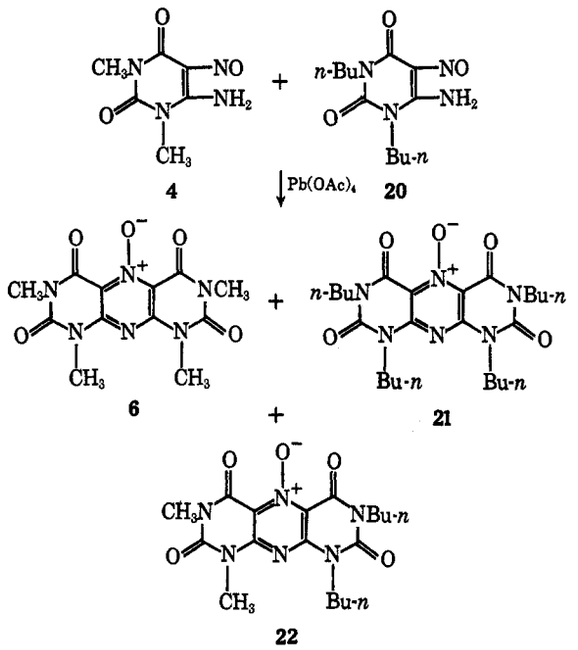
Although a number of different mechanisms (both

(9) H. Kwart and I. M. Sarasohn, *J. Amer. Chem. Soc.*, **83**, 909 (1961).

(10) C. A. Swan and D. G. I. Felton, "Phenazines," Interscience, New York, N. Y., 1957, p 12.

(11) E. M. Burgess and G. Milne, *Tetrahedron Lett.*, 93 (1966).

(12) For example, the 1770-cm^{-1} band exhibited by 1-phenyl-3-acetoxy-5-pyrazolecarboxylic acid has been attributed to the lactim *O*-acetate grouping: Y. Maki, H. Kizu, and K. Obata, *Yakugaku Zasshi*, **83**, 725 (1963).



free radical and ionic) can be written for the lead tetraacetate oxidation of **4** to **6**, we are unable at present to advance evidence favoring any one over the others. Work is underway in an effort to clarify the course of this intriguing transformation.

Experimental Section[13]

Oxidation of 1,3-Dimethyl-6-amino-5-nitrosouracil (4) with Lead Tetraacetate. Formation of 1,3,6,8-Tetramethyl-2,4,5,7-(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-Oxide (6).—To a solution of 13.8 g (0.075 mol) of 1,3-dimethyl-6-amino-5-nitrosouracil (4) in 200 ml of glacial acetic acid was added 33.24 g (0.075 mol) of lead tetraacetate in portions over a period of 5 min. The reaction was mildly exothermic and proceeded with evolution of nitrogen. The color of the reaction mixture had changed from deep violet to pale yellow by the time addition of the lead tetraacetate was complete, and during this period a light yellow crystalline solid separated from the reaction mixture. The mixture was stirred (nitrogen atmosphere) at room temperature for 18 hr to ensure complete reaction and the precipitated pale yellow crystalline solid was collected by filtration, washed well with water, and dried. Recrystallization from a large volume of dimethylformamide with the use of decolorizing charcoal gave 8.0 g (67%) of long yellow needles: mp 360–362° dec; ir 1725, 1680 (br), 1585, 1550 cm^{-1} (br); mass spectrum *m/e* 320, 304 (M − 16).

Anal. Calcd for $C_{12}H_{12}N_6O_5$: C, 45.00; H, 3.78; N, 26.24. Found: C, 45.03; H, 3.98; N, 25.98.

4,6-Dimethyl-5,7(4*H*,6*H*)-furazano[3,4-*d*]pyrimidinedione (5). Method A.—Evaporation to dryness of the acetic acid filtrate above gave an oily residue which, on trituration with water, gave a colorless, crystalline solid. This compound was collected by filtration and recrystallized from acetone to give 2.6 g (19%) of colorless platelets: mp 225–226°; ir 1750, 1700, 1645, 1565 cm^{-1}; nmr (CF_3COOH) δ 3.49 (3 H, N_4 CH_3), 3.60 (3 H, N_6 CH_3); mass spectrum *m/e* 182, 152.

Anal. Calcd for $C_6H_6N_4O_3$: C, 39.56; H, 3.32; N, 30.76. Found: C, 39.32; H, 3.45; N, 30.65.

Method B.—To a suspension of 4.60 g (0.025 mol) of 1,3-dimethyl-6-amino-5-nitrosouracil (4) in 130 ml of benzene was added an equivalent amount of lead tetraacetate in small portions over a period of 6 hr. During this time the reaction mixture was maintained at 60°; some evolution of nitrogen was observed. The reaction mixture was then allowed to stir at room temperature for an additional 24 hr (nitrogen atmosphere). The suspended solids (containing some unreacted **4** as indicated by its red-violet color) were collected by filtration, washed well with water, dried, and recrystallized from dimethylformamide to give 0.40 g of 1,3,6,8-tetramethyl-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-oxide (**6**), mp 361–362° dec, identical with the material obtained above by oxidation of **4** in glacial acetic acid solution. The benzene filtrate was washed with water, dried with anhydrous magnesium sulfate, and evaporated to dryness. The residual solid was recrystallized from acetone to give 2.71 g (60%) of **5** as colorless plates, mp 225–226°, identical in all respects with the compound obtained by oxidation of **4** in glacial acetic acid.

1,3,6,8-Tetramethyl-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]-pteridinetetrone (8).—To a suspension of 0.5 g of **6** in 35 ml of 70% aqueous ethanol was added dropwise at room temperature 0.5 g of sodium dithionite. The reaction mixture was stirred for 2 hr, diluted with 30 ml of water, and filtered. The pale yellow crystals which were collected were recrystallized from glacial acetic acid to give 0.5 g of **8**, mp 385°, identical in all respects (ir, nmr, melting point, and mixture melting point) with an authentic sample.[6]

Alkaline Hydrolysis of 1,3,6,8-Tetramethyl-2,4,5,7(1*H*,3*H*,-6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-Oxide (6).—A suspension of 4.00 g of **6** in 50 ml of 4 *N* sodium hydroxide solution was warmed gently with swirling at 60–70°. As the hydrolysis proceeded, the reaction mixture first formed a hard mass and then became pasty. After about 1 hr, the alkaline mixture was cooled to room temperature and the light yellow solid which separated was collected by filtration, washed well with water, and dried. Recrystallization of the collected solid from aqueous dimethylformamide gave 1.50 g (50%) of **1,3-dimethyl-5-methylaminocarbonyl-6-methylamino-1*H*-imidazo[4,5-*b*]pyrazin-2(3*H*)-one (12)** as pale yellow crystals: mp 355° dec; ir 3390, 3310 (NH), 1695 (imidazolone C=O), 1650 cm^{-1} (amide C=O); nmr (CF_3COOH) δ 3.30, 3.14, 3.00, 2.86; mass spectrum *m/e* 250.

Anal. Calcd for $C_{10}H_{14}N_6O_2$: C, 47.99; H, 5.64; N, 35.58. Found: C, 47.90; H, 5.71; N, 35.56.

The monoacetate of **12**, prepared by heating with acetic anhydride, was recrystallized from acetone: mp 295° dec; ir 3325 (NH), 1710 (imidazolone C=O), 1690 (acetyl C=O), 1670 cm^{-1} (amide C=O).

The aqueous dimethylformamide mother liquors obtained as described above were concentrated to dryness and the solid residue was recrystallized from acetone to give 0.65 g (20%) of **3,5-bis(methylamino)-*N*,*N*′-dimethylpyrazine-2,6-dicarboxamide 1-oxide (10)**, in the form of long yellow needles: mp 158–159°; mass spectrum *m/e* 268, 252 (M − 16); ir 3350, 3150 (NH), 1650 cm^{-1} (amide C=O); nmr (CF_3COOH) δ 2.99, 3.32 (N CH_3).

The alkaline filtrate of the initial hydrolysis mixture, obtained as described above, was acidified at 0° with concentrated hydrochloric acid. The precipitated amorphous solid was recrystallized from methanol to give 0.64 g (20%) of **3,5-bis(methylamino)-6-carboxy-*N*-methylpyrazine-2-carboxamide 1-oxide (11)**, in the form of pale yellow feathery crystals: mp 218° dec; mass spectrum *m/e* 255, 239 (M − 16); ir 3345, 3250 (NH), 3200–3000 (br, carboxyl OH), 1695 (carboxyl C=O), 1650 cm^{-1} (amide C=O).

Anal. Calcd for $C_9H_{13}N_5O_4$: C, 42.35; H, 5.13; N, 27.44. Found: C, 42.09; H, 5.11; N, 27.10.

3,5-Bis(methylamino)-*N*,*N*′-dimethylpyrazine-2,6-dicarboxamide (9).—A mixture of 0.20 g of 3,5-bis(methylamino)-*N*,*N*′-dimethylpyrazine-2,6-dicarboxamide 1-oxide (**10**) and 20 ml of triethyl phosphite was heated under reflux for 3 hr. Excess triethyl phosphite was then removed by distillation *in vacuo*, and the residue was dissolved in chloroform–acetone (8:2) and chromatographed on silica gel. The column was diluted with additional chloroform–acetone (8:2), the eluate was evaporated to dryness, and the residue was recrystallized from acetone to give 0.066 g (35%) of **9**, mp 232°, as bright yellow crystals. The product was identical in all respects (ir, nmr, melting point, and mixture melting point) with an authentic sample of **9**.[6,14]

3,5-Bis(methylamino)-6-carboxy-*N*-methylpyrazine-2-carboxamide (13).—A mixture of 0.20 g of 3,5-bis(methylamino)-6-carboxy-*N*-methylpyrazine-2-carboxamide 1-oxide (**11**) and 0.45 g of sodium dithionite in 40 ml of 70% aqueous ethanol was heated with stirring at 90° for 3 hr. After cooling and acidifying

(13) Melting points are uncorrected and were determined on a Thomas-Hoover apparatus. Infrared data refer to Nujol mull spectra taken on a Perkin-Elmer Model 237B grating infrared spectrometer. Nmr data were obtained on a Varian A-60A instrument, using TMS as internal standard.

(14) Belgium Patent 568,115 (J. R. Geigy S. A.), May 29, 1957.

with hydrochloric acid, the reaction mixture was concentrated to a small volume under reduced pressure. On standing overnight, a yellow crystalline solid separated which was collected by filtration and recrystallized from alcohol to give 0.10 g (56%) of **13**: mp 190°;[15] ir 3425–3100 (NH and carboxyl OH), 1725 (carboxyl C=O), 1675 cm^{-1} (amide C=O).

Anal. Calcd for $C_9H_{13}N_5O_3$: C, 45.18; H, 5.48; N, 29.28. Found: C, 44.82; H, 5.71; N, 29.50.

3,5-Bis(methylamino)-*N*-methylpyrazine-2-carboxamide 1-Oxide (14).—To 5 ml of trifluoroacetic acid was added 0.50 g of 3,5-bis(methylamino)-6-carboxy-*N*-methylpyrazine-2-carboxamide 1-oxide (**11**) and the mixture was swirled at room temperature. Rapid decarboxylation took place, as evidenced by vigorous evolution of CO_2. The trifluoroacetic acid was removed by evaporation under reduced pressure and the solid residue was recrystallized from ethanol to give 0.32 g (77%) of pale yellow crystals of **14**: mp 235–236°; ir 3325, 3250, 3150 (NH), 1650 cm^{-1} (amide C=O); nmr ($DCCl_3$) δ 2.95, 3.03, 3.09 (N CH_3), 6.99 (1 H, C_6 H).

3,5-Bis(methylamino)-*N*-methylpyrazine-2-carboxamide (15). Method A.—A mixture of 0.50 g of 3,5-bis(methylamino)-*N*-methylpyrazine-2-carboxamide 1-oxide (**14**) and 0.8 g of sodium dithionite in 50 ml of water was heated under reflux for 2.5 hr with stirring. The cooled reaction mixture deposited yellow crystals which were collected by filtration and recrystallized from water to give 0.31 g (67%) of **15**: mp 151–152°; ir 3400, 3350 (NH), 1650 cm^{-1} (amide C=O); nmr ($DCCl_3$) δ 2.85, 2.93, 3.01 (N CH_3), 7.06 (1 H, C_6 H).

Anal. Calcd for $C_8H_{13}N_5O$: C, 49.23; H, 6.67; N, 35.89. Found: C, 49.26; H, 6.96; N, 35.86.

Method B.—**14** (300 mg) was heated at 190–200° (0.25 mm). The residual solid was extracted with hot water, and the extract was treated with charcoal, filtered, and concentrated to a small volume. Cooling resulted in the separation of 0.05 g of **15**, identical in all respects with the product obtained by method A.

Treatment of 1,3,6,8-Tetramethyl-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-Oxide (6) with Acetic Anhydride. Formation of 16.—A mixture of 2.0 g of **6** was heated under reflux with 20 ml of acetic anhydride for 20 hr. As the reaction proceeded, the suspended solid gradually went into solution and the color of the reaction mixture changed from yellow to light brown. A small amount of unreacted **6** was removed by filtration, and the clear acetic anhydride filtrate was allowed to stand at room temperature for several hours. Filtration then gave 0.5 g of 1,3,6,8-tetramethyl-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]-pteridinetetrone (**8**), identical with an authentic sample prepared as described above by sodium dithionite reduction of **6**. Concentration of the acetic anhydride filtrate and recrystallization of the solid residue from ethanol then gave 0.6 g (40%) of **16**: mp 248°; mass spectrum *m/e* 263; ir 1825 (oxazolidone C=O), 1720, 1675 cm^{-1} (uracil C=O); nmr ($DCCl_3$) δ 3.7, 3.55, 3.5 (N CH_3).

Anal. Calcd for $C_{10}H_9N_5O_4$: C, 45.63; H, 3.45; N, 26.61. Found: C, 45.94; H, 3.63; N, 26.62.

1,3-Dimethyl-6-hydroxy-7-methylaminolumazine (18).—A suspension of 0.3 g of **16** in 30 ml of 50% aqueous ethanol was heated under reflux for 1 hr. The reaction mixture was concentrated to dryness and the residual solid was recrystallized from glacial acetic acid to give 0.2 g of **18** as fine colorless crystals: mp 370° dec; ir 3320, 3160 (NH), 1710, 1680 (uracil C=O), 1655 cm^{-1} (C_6 C=O); nmr (CF_3COOH) δ 3.80, 3.58, 3.28 (N CH_3).

(15) This compound has previously been reported (as the hemihydrate) to melt at 214° dec (ref 14).

1,3-Dimethyl-6-acetoxy-7-(*N*-methylacetamido)lumazine (19).—This compound was prepared in quantitative yield by refluxing **18** with acetic anhydride in the presence of anhydrous potassium acetate. Recrystallization of the crude product from methanol–ether (1:1) gave colorless crystals: mp 165°; ir 1775 (lactim *O*-acetate), 1730, 1675 cm^{-1} (br, uracil and amide C=O).

Anal. Calcd for $C_{13}H_{15}N_5O_5$: C, 48.59; H, 4.68; N, 21.78. Found: C, 48.67; H, 4.89; N, 21.79.

1,3,6,8-Tetra(*n*-butyl)-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-Oxide (21).—A solution of 5.26 g (0.02 mol) of 1,3-di(*n*-butyl)-6-amino-5-nitrosouracil (**20**) in 100 ml of glacial acetic acid was treated in small portions with 8.8 g (0.02 mol) of lead tetraacetate. The reaction was mildly exothermic and proceeded with evolution of nitrogen. After addition of lead tetraacetate was complete, the reaction mixture was stirred at room temperature (nitrogen atmosphere) for 18 hr and then concentrated to dryness under reduced pressure. The oily residue was triturated with water to give a solid mass which was pressed dry on a filter and recrystallized from acetone to give 3.70 g (90%) of pale yellow crystals of **21**: mp 158°; mass spectrum *m/e* 489, 473 (M − 16); ir 1725, 1680 cm^{-1}.

Anal. Calcd for $C_{24}H_{36}N_6O_5$: C, 59.00; H, 7.43; N, 17.20. Found: C, 58.87; N, 7.32; N, 17.34.

Lead Tetraacetate Oxidation of a Mixture of 1,3-Dimethyl- and 1,3-Di(*n*-butyl)-6-amino-5-nitrosouracil (4 and 20).—A mixture of 1.84 g (0.01 mol) of 1,3-dimethyl-6-amino-5-nitrosouracil (**4**) and 2.68 g (0.01 mol) of 1,3-di(*n*-butyl)-6-amino-5-nitrosouracil (**20**) in 70 ml of glacial acetic acid was treated with 8.8 g (0.02 mol) of lead tetraacetate in small portions over a period of 15 min. The reaction mixture was then stirred under nitrogen for 24 hr. Cooling of the crude reaction mixture resulted in the separation of 0.30 g of **6**, mp 360–362° dec, identical with authentic **6** prepared as described above. The filtrate was evaporated to dryness under reduced pressure and the residue was triturated with water to dissolve excess lead tetraacetate. The suspended solids were collected by filtration and dissolved in 30 ml of hot acetone. The acetone solution was allowed to stand at room temperature for several hours and filtered to remove a small amount of an insoluble impurity, and the filtrate was diluted with 20 ml of chloroform. The solution thus obtained was chromatographed on silica gel and the column was eluted with chloroform–acetone (7:3) to give the following compounds, listed in their order of elution: 4,6-dimethyl-5,7(4*H*,6*H*)-furazano[3,4-*d*]pyrimidinedione (**5**) (0.21 g), 1,3,6,8-tetra(*n*-butyl)-2,4,5,7-(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-oxide (**21**) (0.90 g), and **1,3-dimethyl-6,8-di(*n*-butyl)-2,4,5,7-(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-oxide (22)** (0.19 g). Recrystallization of the latter compound from acetone gave pale yellow crystals: mp 203°; mass spectrum *m/e* 388, 372 (M − 16); ir 1725, 1675 cm^{-1} (br, uracil C=O).

Anal. Calcd for $C_{13}H_{24}N_6O_5$: C, 53.45; H, 5.98; N, 20.78. Found: C, 53.55; H, 5.91; N, 20.57.

Further elution of the column with chloroform–ethanol (1:1) gave an additional 0.22 g of **6**.

Registry No.—**4,** 6632-68-4; **5,** 33070-47-2; **6,** 33070-48-3; **10,** 33070-49-4; **11,** 33070-50-7; **12,** 33070-51-8; **12** monoacetate, 33070-52-9; **13,** 33122-32-6; **14,** 33070-53-0; **15,** 33070-54-1; **16,** 33070-55-2; **18,** 33070-56-3; **19,** 33070-57-4; **21,** 33070-58-5; **22,** 33070-59-6; lead tetraacetate, 546-67-8.