Anal. Calcd for $C_8H_9NO_4 \cdot HCl$: C, 43.75; H, 4.59; N, 6.38. Found: C, 43.84; H, 4.73; N, 6.42.

4′,5′-(Dimethoxyoxime)-3-hydroxy-2-methylpyridine (*o*-Pyridoxidial Dimethoxyoxime) (XI).—To a solution of 204 mg (2.4 mmol) of methoxyamine hydrochloride in 20 ml of distilled water 220 mg (1 mmol) of *o*-pyridoxidial hydrochloride (X), dissolved in 10 ml of distilled water, was added drop by drop with stirring. After the addition was complete, 500 mg of sodium acetate dissolved in 10 ml of distilled water was added to bring the reaction mixture to pH 5–6. The mixture was cooled in a refrigerator and the precipitated oxime was filtered and recrystallized from an ethanol–water mixture to yield 198 mg (88.5%) of white, needle-shaped crystals of dimethoxyoxime (XI): mp 106–107°; $\lambda_{max}^{0.1\ N\ HCl}$ 331 mμ (sh) (ε 8.5 × 10³), 311 (11.3 × 10³), 305 (sh) (11.0 × 10³), and 243 (16.8 × 10³); $\lambda_{max}^{0.1\ N\ NaOH}$ 362 mμ (ε 7.8 × 10³) and 236 (20.2 × 10³).

Anal. Calcd for $C_{10}H_{13}N_3O_3$: C, 53.80; H, 5.87; N, 18.82. Found: C, 54.04; H, 5.37; N, 19.16.

4′,5′-Bisthiosemicarbazone-3-hydroxy-2-methylpyridine (*o*-Pyridoxidial Bisthiosemicarbazone) (XII).—A solution of 220 mg of *o*-pyridoxidial hydrochloride (X) in 5 ml of distilled water was added drop by drop with stirring to the warm solution of 250 mg of thiosemicarbazide in 10 ml of distilled water. After adding 170 mg of sodium acetate, the reaction mixture was allowed to cool, whereupon 200 mg (64.3%) of crude bisthiosemicarbazone precipitated out. A portion was recrystallized from 95% ethanol and dried over phosphorous pentoxide at 80° under high vacuum when an orange red compound, mp 172–174° dec, was obtained.

Anal. Calcd for $C_{10}H_{13}N_7OS_2 \cdot H_2O$: C, 36.46; H, 4.59; N, 29.76; S, 19.46. Found: C, 37.26; H, 4.33; N, 30.16; S, 19.89.

1,3-Dihydro-1,3-dimethoxy-6-methyl furo[3,4-*c*]pyridin-7-ol[39] (*o*-Pyridoxidial Dimethyl Acetal) (XIII).—*o*-Pyridoxidial hydrochloride (X) (0.5 g) dissolved in 50 ml of anhydrous methanol[33] was heated with protection from moisture in an oil bath and kept at 50–60° for 5 days. The reaction mixture was cooled, ammonia gas was bubbled into it, and then it was concentrated to a very small volume. Excess of ether was added and the mixture was filtered. The filtrate was evaporated to dryness, the residue was extracted with chloroform, the extract was concentrated to about 50 ml, and excess of petroleum ether was added to it. The mixture was kept in a refrigerator overnight, yielding the dimethyl acetal XIII. It was recrystallized four times with chloroform–petroleum ether mixture to yield 0.215 g (44.8%): mp 164–165°; $\lambda_{max}^{0.1\ N\ HCl}$ 288 mμ (ε 9.3 × 10³) and 227 (3.8 × 10³); $\lambda_{max}^{0.1\ N\ NaOH}$ 304 mμ (ε 8.1 × 10³) and 241 (9.7 × 10³).

Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.86; H, 6.20; N, 6.63. Found: C, 57.13; H, 6.25; N, 6.61.

Sodium Borohydride Reduction of 4,5-Diformyl-3-hydroxy-2-methylpyridine Hydrochloride (*o*-Pyridoxidial Hydrochloride) (X).—Over a period of 15 min, a solution of 100 mg of *o*-pyridoxidial hydrochloride (X) in 5 ml of 90% methanol was added drop by drop with stirring to a solution of 50 mg of sodium borohydride in 5 ml of 0.1 *N* methanolic sodium hydroxide. In another 15 min of stirring the reaction was complete. The excess of sodium borohydride was decomposed with a few drops of concentrated hydrochloric acid. The solution was evaporated to dryness under reduced pressure; the solid residue extracted twice with 5-ml portions of absolute ethanol and filtered. To the filtrate excess of anhydrous acetone was added and the mixture was kept overnight in a refrigerator yielding 80 mg (85%) of needle-shaped crystals. This compound was identified as pyridoxol hydrochloride (XIV), based upon its melting point and mixture melting point of 208–209° with an authentic sample and its ultraviolet and infrared spectra which were found to be identical with those of the authentic sample. Pyridoxol was also obtained when pyridoxal and isopyridoxal were treated with sodium borohydride under the conditions described above.

Registry No.—III, 15833-01-9; V, 15833-02-0; VI, 15833-03-1; VII, 15833-04-2; VIII, 15833-05-3; IX, 15832-16-3; X, 15832-17-4; XI, 15832-18-5; XII, 15832-19-6; XIII, 15832-20-9.

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N-Vinyl Derivatives of Substituted Pyrimidines and Purines[1]

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The preparation of potentially polymerizable compounds containing heterocyclic moieties of nucleic acids is described. 1-Vinyluracil was prepared by dehydrochlorination of 1-(2-chloroethyl)uracil (**3**). 1-Vinyl-3-methyluracil, 1-vinyl-4-ethoxy-2-pyrimidinone (**7**), 6-chloro-9-vinylpurine (**8**), and 2,6-dichloro-9-vinylpurine (**9**) were prepared from the unsubstituted heterocycles by a vinyl interchange reaction with vinyl acetate, catalyzed by mercuric acetate and sulfuric acid.

The importance of nucleic acids has resulted in many studies on their intramolecular forces using model systems.[2,3] Among possible model systems are polymers containing the heterocyclic moieties of nucleic acids but differing from them in the connecting backbone. To date only a few papers have been published on such models. The necessary macromolecules were usually prepared by attaching heterocycles to cellulose derivatives.[4–9] Only recently Cassidy and Jones[10] described the preparation and properties of polymers based on 5′-O-acrylthymidine. In our laboratory, a program has been started in this direction. The present paper describes the preparation of the N-vinyl derivatives of substituted pyrimidine and purine heterocycles with substituents suitable for subsequent conversion into heterocycles of nucleic acids (uracil, cytosine, adenine and guanine). This approach avoids possible difficulties with functional groups (*e.g.*, the amino group) during the polymerization reaction. N-Vinyl polymers were chosen since they have been well studied and because related poly-

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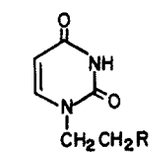
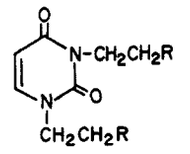
mers of N-vinylpyrrolidinone and N-vinyl-2-oxazolidinone are reasonably soluble in water.[11,12] As the intended physicochemical and biological studies on these compounds may require relatively large amounts of material, different routes to the desired products were tested.

For the uracil series the simplest monomer is 1-vinyluracil. Two approaches for synthesis of this compound were adopted. The first approach is by means of an appropriate elimination reaction, starting from the known[13,14] 1-(2-hydroxyethyl)-uracil. This compound (**1**) was prepared by Prystas and Gut[13] by treating uracil with ethylene carbonate and subsequent separation from the accompanying disubstituted derivative (**2**) by chromatography. We modified the reaction for large-scale preparation and tested other approaches for the separation of the mixture. Recrystallization does not give good results and the separation through salt formation procedure is not practical, as the compound **2** is rather hydrophilic. Eventually we found that by addition of excess reagent it is possible to convert the mixture nearly quantitatively into the corresponding chlorides **3** and **4** or the acetates **5** and **6**, and, as the properties of these derivatives are very different, the separation by crystallization is easy. For the preparation of 1-vinyluracil, the most practical procedure was found to be the dehydrochlorination of **3** with potassium *t*-butoxide in dimethyl sulfoxide at room temperature.[15] Other dehydrochlorination procedures for **3**, such as reaction with potassium *t*-butoxide in boiling *t*-butyl alcohol[16] or reaction with alkalies under conditions successfully used for preparation[17] of N-vinyl pyrrolidinone, gave very low yields. Pyrolysis of acetate **5**, a procedure which requires the temperature to be above 600°, also produced only a small amount of 1-vinyluracil with most of the starting material unchanged. We also tested acidic dehydration of **1** at 180° but the yield of the vinyl compound is very low. Another synthetic approach is the vinyl interchange reaction with vinyl acetate catalyzed by mercuric acetate and sulfuric acid;[18] such a reaction was successful with a few heterocycles.[19] An attempt was made first on the vinylation of 3-substituted derivatives of uracil, such as 3-methyluracil. The latter compound was prepared by a new route—methylation of 1-acetyluracil with diazomethane and subsequent hydrolysis. The vinylation procedure gave 1-vinyl-3-methyluracil which was identical with the substance prepared by diazomethane from 1-vinyluracil; the structure **1** previously proposed on the basis of spectral data[13] is thus confirmed by a chemical method. However, the vinylation reactions on 3-benzoyluracil and uracil were not successful.

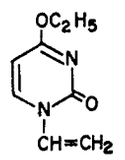
For the cytosine series the simplest monomer would be 1-vinylcytosine with the amino group blocked. Attempts to prepare such a compound by vinylation



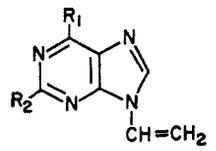
1, R=OH
3, R=Cl
5, R=OCOCH$_3$



2, R=OH
4, R=Cl
6, R=OCOCH$_3$



7



8, R$_1$=Cl , R$_2$=H
9, R$_1$=R$_2$=Cl

of N-acetylcytosine or cytosine were unsuccessful. Fortunately, vinylation was found to be applicable to 4-ethoxy-2-pyrimidinone.[20] The starting compound can exist in two tautomeric forms—1H and 3H; similarly there are two possible N-vinyl derivatives. However, only one product was isolated. Hydrogenation and hydrolysis of this product gave 1-ethyl-5,6-dihydrouracil; the structure therefore must be as given by formula **7**; the N-vinyl derivative of the predominant tautomeric form.[21,22] The polymer prepared from vinyl compound **7** can be the starting material for both the uracil and cytosine series; both amination and hydrolysis of a 4-ethoxy group has been previously demonstrated for the 4-ethoxy-2-pyrimidinone[20] and its N-1-ribosyl derivative.[23]

For the purine series, chlorine-substituted heterocycles were chosen as starting materials. The reason for this choice is that 6-chloro-9-ethylpurine can be converted into 9-substituted derivatives of adenine or hypoxanthine;[24] and the 2,6-dichloro derivatives probably can be converted into guanine derivatives due to the large difference in reactivity of these two chlorine atoms.[25,26] Vinylation of 6-chloro- and 2,6-dichloropurine gave good yields of vinyl derivatives. Again there are two possibilities for the vinyl substitution, namely, at positions 7 or 9. Since the addition of similarly substituted purines to dihydropyran has been found to furnish mainly the 9-substituted derivatives,[27] it appears likely that the vinylation reaction, which starts probably by an addition of the heterocycle or its mercury derivatives to the vinyl double bond,[28,29] would also yield 9-substituted compounds. This hypothesis was confirmed by hydrogenation of the isolated vinyl derivatives **8** and **9**. Both compounds yielded 9-ethylpurine as the reaction product which proves that the designated structures for the vinyl derivatives **8** and **9** are correct.

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The study of polymerization reactions of all five vinyl derivatives is presently underway in our laboratory.

Experimental Section

Melting points were determined on the hot stage and are corrected. Purity of compounds was checked by chromatography, using either a descending system on Whatman No. 40 paper or an ascending system on silica gel, Eastman Sheet 6060.

The compounds were located by their absorption of ultraviolet light.

Water saturated 1-butanol was used as eluent for all the chromatographic systems including the column chromatography described in later sections.

Ultraviolet spectra were measured in a Cary 15 spectrophotometer. Spectra were taken within 12 min from the time of addition of the compound to the solvent, and then repeated three times at 5-min intervals to ensure that no change occurs owing to decomposition during measurement. Pyrimidines were dissolved in phosphate buffer (0.05 *M* in phosphate, pH 7) and purines were dissolved in 95% ethanol since the amount of purines dissolved in aqueous buffer within a 12-min period was usually too low for the measurement.

Microanalyses were by Spang Microanalytical Laboratory, Inc., Ann Arbor, Mich., and Galbraith Laboratories, Inc., Knoxville, Tenn.

1-(2-Hydroxyethyl)uracil (1) and 1,3-Di(2-hydroxyethyl)uracil (2).—Uracil (89.6 g) and its monosodium salt (2 g) were dissolved in dry, hot dimethylformamide (1300 ml). To the boiling stirred solution, ethylene carbonate (72 g) in dimethylformamide (150 ml) was added dropwise. After boiling for 1 hr the solution was evaporated *in vacuo* (60°). Ethanol was added and the mixture was repeatedly evaporated *in vacuo* to remove the remaining dimethylformamide. The residue was dissolved in hot water (700 ml). The addition of Dowex 50 W (H^+ form) brought the solution to pH 5. After filtration, the solvent was removed *in vacuo* and the residue extracted with 1 l. of boiling ethanol; most of the uracil remained undissolved. The mixture was filtered; evaporation of the filtrate gave white crystals of **1** and **2** and a small quantity of uracil. A crystalline mixture of **1** and **2** (85 g) was obtained following extraction with ethyl acetate in a Soxhlet apparatus. This mixture was separated by column chromatography on cellulose; Prystas and Gut[13] used a 1:150 ratio of substance–cellulose; we found that it can be reduced to 1:50. The melting points of separated **1** (138°) and **2** (154°) corresponded to the published values.[13,14]

1-(2-Chloroethyl)uracil (3).—Pyridine (0.5 ml) was added to a solution of a mixture of **1** and **2** (16 g) in dry, hot dioxane (350 ml). Thionylchloride (30 ml) in dioxane (20 ml) was added dropwise and the solution was boiled for 1 hr. The solvent was then evaporated *in vacuo* and the residue was dissolved in 800 ml of chloroform. The chloroform solution was filtered and the filtrate extracted three times by 50 ml of water. The organic phase was dried (magnesium sulfate), filtered, and evaporated and the residue dissolved in hot dioxane. After cooling, *ca.* 6 g of crystals was collected and recrystallized from dioxane, mp 164–167° (identical with the melting point of the substance reported by Prystas and Gut[13]). The water extracts contained a mixture of **1** and **3** which can be recycled. It is interesting to note the difference in reactivity between **1** and uracil-1-acetic acid with respect to thionyl chloride. The former reacts at room temperature, whereas attempts of our own and others[30] to convert the acid into the chloride were unsuccessful.

1,3-Di(2-chloroethyl)uracil (4).—The dioxane mother liquors obtained from the crystallization of **3** were evaporated. The residue was dissolved in chloroform, extracted first by 1 *N* sodium hydroxide and then by water, and dried (magnesium sulfate). A colorless oil was obtained after evaporation which distilled at a bath temperature of 160° (0.07 mm). The identical substance was prepared from the pure diol **2** by thionylchloride.

Anal. Calcd for $C_8H_{10}N_2O_2Cl_2$: C, 40.53; H, 4.25; N, 11.82. Found: C, 40.31; H, 4.24; N, 12.05.

1-(2-Chloroethyl)-3-methyluracil.—This compound was prepared from **3** by reaction with excess diazomethane in ether–dioxane solution for 5 days at room temperature. It was recrystallized from water, mp 88–89°.

Anal. Calcd for $C_7H_9N_2O_2Cl$: C, 44.57; H, 4.81; N, 14.85. Found: C, 44.63; H, 4.94; N, 14.95.

1-(2-Acetoxyethyl)uracil (5).—A suspension of **1** and **2** (obtained from Soxhlet extraction, 10 g) was stirred overnight in acetic anhydride (200 ml) and pyridine (0.1 ml). Methanol was added to the clear solution, which was evaporated *in vacuo*. The residue was dissolved in hot ethyl acetate and cooled; white crystals (5 g) of **5** were obtained. These were recrystallized from ethyl acetate and ethanol, mp 136–138°. The identical substance was prepared by similar acetylation of the pure alcohol **1**.

Anal. Calcd for $C_8H_{10}N_2O_4$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.43; H, 5.07; N, 14.14.

1,3-Di(2-acetoxyethyl)uracil (6).—The ethyl acetate mother liquor obtained from the crystallization of **5** was evaporated. The residue was treated by an identical procedure described for the preparation of compound **4**. After the evaporation of the dried chloroform, a yellow oil which slowly crystallized was obtained: bp 180° (bath) (0.07 mm); mp 50–52°. The identical substance was prepared by acetylation of the pure diol **2**.

Anal. Calcd for $C_{12}H_{16}N_2O_6$: C, 50.70; H, 5.67. Found: C, 51.23; H, 5.97.

1-(2-Acetoxyethyl)-3-methyluracil.—This compound was prepared from **5** by reaction with diazomethane in ether–dioxane solution for 5 days. A colorless oil, distilled at a bath temperature of 160° (0.07 mm), was obtained.

Anal. Calcd for $C_9H_{12}N_2O_4$: C, 50.94; H, 5.70. Found: C, 50.81; H, 5.86.

1-Vinyluracil.—The chloride **3** (2.5 g) was dissolved in dry dimethyl sulfoxide (20 ml) and added dropwise to the stirred solution of 5.1 g of potassium *t*-butoxide in 20 ml of dimethyl sulfoxide. After an hour at room temperature, 60 ml of cold water was added and the solution was made slightly acidic by adding Dowex 50 W (H^+ form). The filtered solution was evaporated *in vacuo* (0.1 mm) under 60°. A crop of crystals was obtained which was recrystallized from ethanol. This procedure gave 1.2 g of 1-vinyluracil (yield 60%) contaminated by alcohol **1**. The pure compound was prepared by chromatography on cellulose (50 g). The vinyl compound (eluted before the alcohol) sublimed *in vacuo:* mp 188–189°; λ_{max} (buffer, pH 7) 277 mμ (ε 10,800) and 223 mμ (ε 10,400); λ_{min} 245 mμ; λ_{max} (0.01 *N* sodium hydroxide) 277 mμ (ε 10,100) and 222 mμ (ε 11,600); λ_{min} 252 mμ, shoulder 232 mμ.

Anal. Calcd for $C_6H_6N_2O_2$: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.05; H, 4.37; N, 20.38.

1-Vinyl-3-methyluracil.—1-Vinyluracil (35 mg) was dissolved in methanol (3 ml) and excess diazomethane in ether was added. After 24 hr the solution was evaporated and the residue was chromatographed on a 2-mm layer of silica gel. The main ultraviolet light absorbing zone was eluted. Crystals were obtained after evaporation and were sublimed *in vacuo:* mp 92–94°; infrared spectrum identical with that of the 1-vinyl-3-methyluracil prepared by the vinylation reaction.

Pyrolysis of Acetate 5.—A vycor glass tube, sealed at one end, was loaded with 1.4 g of acetate **5**, 30 mg of hydroquinone, and Vycor glass fillings (20-cm zone). The part with glass fillings was placed into furnace maintained at 620°; the tube was evacuated to 10 mm; and acetate **5** was distilled slowly throughout the heated zone. A brown distillate was collected, treated with charcoal in ethanol, and fractionally recrystallized from ethanol. Considerable amount of starting acetate (600 mg) was recovered; the other fractions gave, by chromatography on cellulose, 0.1 g (10%) of 1-vinyluracil, which was identical with the substance prepared from the dehydrochlorination experiment.

3-Methyluracil.—1-Acetyluracil was prepared by the method of Spector and Keller[31] from uracil and acetic anhydride. This compound (13 g) was dissolved in 200 ml of hot dioxane. Then, using a Dry Ice condenser, an ethereal solution of diazomethane was added in excess. After 1 day the mixture was evaporated, the residue was dissolved in 45 ml of ethanol, and 45 ml of 0.25 *M* HCl, and the solution boiled for 1 hr. According to chromatography, both uracil and 3-methyluracil were present; the mixture was separated by fractional sublimation (140°, 0.05 mm) to give 3-methyluracil as the sublimate (8 g, 75% yield), mp 179–183°, identical with the sample prepared by a known route.[32]

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3-Benzoyluracil was prepared by hydrolysis of 1,3-dibenzoyluracil.[33] In our hands it had mp 216° dec instead of 198–201° reported previously.[33]

As the melting point (151–152°) of the reaction product of our compound with diazomethane is the same as that of the 1-methyl-3-benzoyluracil,[33] this difference in the reported melting point may be due to a difference in the rate of heating.

Vinylation Reaction. General Procedure.—A solution of 0.1 ml of concentrated sulfuric acid in ethyl acetate (2 ml) was added to a suspension of 0.5 g of mercuric acetate in 100 ml of vinyl acetate in a pressure flask; a clear solution was formed. This procedure avoids the coloring of vinyl acetate by the direct addition of acid. Then the powdered heterocyclic compound (about 2 g) was added followed by another 50 ml of vinyl acetate. After bubbling with nitrogen for 10 min the flask was closed and placed in a bath at 45–50° with occasional agitation for 1–5 days. After the specified period, dry sodium acetate was added, and the mixture stirred for 10 min and then filtered. The filtrate was evaporated *in vacuo* and the residue was dissolved in chloroform. The solution was then extracted with cold 1 *N* sodium hydroxide; occasionally centrifugation was necessary to facilitate the removal of the aqueous layer. The chloroform layer was dried (magnesium sulfate) and evaporated. The residue was purified by recrystallization and sublimation *in vacuo*. Yields of the vinyl compounds varied; the governing factors[28] appear to be the rate of the solution of the starting material which is difficult to control and the rate of the competing decomposition. All procedures reported below have been repeated successfully several times.

A. 3-Methyluracil.—The reaction time was 6 days. 1-Vinyl-3-methyluracil was recrystallized from cyclohexane: mp 95–97°; λ_{max} (buffer pH 7) 276 mμ (ε 10,500) and 221 mμ (ε 10,500); λ_{min} 246 mμ. In another experiment the reaction time was 10 days; the main portion of the product was polymerized.

Anal. Calcd for $C_7H_8N_2O_2$: C, 55.26; H, 5.30; N, 18.41. Found: C, 55.04; H, 5.51; N, 18.04.

B. 3-Benzoyluracil was sparingly soluble in the vinylation solution and the reaction gave brown products of polymerization and decomposition.

C. Uracil, cytosine, and N-acetylcytosine in the vinylation reaction gave small quantities of oily materials which were not homogeneous; infrared and ultraviolet spectra indicated that only minute quantities of vinylsubstituted heterocycles were present.

D. 4-Ethoxy-2-pyrimidinone was prepared according to Hilbert and Jansen;[20] the purity was checked by paper chromatography using described elution systems.[21,22] Vinylation (2 days) of 1.1 g gave 0.7 g (55%) N-1 vinyl derivative **7**: white crystals (cyclohexane); mp 77–78°; λ_{max} (buffer pH 7) 287 mμ (ε 8600) and 211 mμ (ε 13,600); λ_{min} 251 mμ.

Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.96; H, 5.95; N, 16.99.

E. 6-Chloropurine.—Vinylation (5 days) of 2 g of the starting compound gave 1.6 g (70%) of 6-chloro-9-vinylpurine **8** that was recrystallized from ethanol: mp 166–167°; λ_{max} (95% ethanol) 263 mμ (ε 7500) and 224 (ε 25,700); λ_{min} 249 mμ.

Anal. Calcd for $C_7H_5N_4Cl$: C, 46.55; H, 2.79; N, 31.02. Found: C, 46.55; H, 2.70; N, 31.36.

F. 2,6-Dichloropurine.—Reaction time was 2 days; 1.4 g (80%) of crystalline vinyl compound **9** was obtained from 1.5 g of starting material. This was recrystallized from ethanol: mp 126–127°; λ_{max} (95% ethanol) 274 mμ (ε 7800) and 228 mμ (ε 27,600); λ_{min} 252 mμ, shoulder at 235 mμ.

Anal. Calcd for $C_7H_4N_4Cl_2$: C, 39.09; H, 1.87; N, 26.05. Found: C, 39.58; H, 1.49; N, 25.89.

Hydrogenation of 6-Chloro-9-vinylpurine (8) and of 2,6-Dichloro-9-vinylpurine (9).—Magnesium oxide (45 mg) and palladium on charcoal (5%, 45 mg) were added to a 20-ml solution of ethanol–water (v/v 1:1) containing 90 mg of the chloro derivative. The solution was hydrogenated at room temperature and atmospheric pressure; the consumption of hydrogen practically stopped after 1 hr when the theoretical amount was consumed. The mixture was filtered and 150 mg of potassium carbonate was added to the filtrate which was then evaporated. The residue was extracted with carbon tetrachloride and the resulting extract was dried (magnesium sulfate).

Crystalline 9-ethylpurine was obtained after evaporation of the extract; it gave an infrared spectrum identical with that of the authentic sample.[34] In preliminary experiments, acetone was used for extraction; crystallization was very slow.

Hydrogenation and Hydrolysis of 1-Vinyl-4-ethoxy-2-pyrimidinone (7).—Hydrogenation was conducted as described immediately above with 90 mg of vinyl compound in 20 ml of ethanol–water solution (1:1 v/v) containing 45 mg of palladium on charcoal (5%). The filtered solution was evaporated *in vacuo;* the residue was dissolved in 20 ml of hydrochloric acid (1 *N*), left overnight, and again evaporated. After sublimation *in vacuo*, the infrared spectrum of the sublimate was identical with the spectrum of 1-ethyl-5,6-dihydrouracil. The compound for comparison was purchased from Cyclo Chemical Corp., Los Angeles, Calif., and was purified by vacuum sublimation.

The product of hydrogenation and hydrolysis was shown by paper chromatography to contain a very small amount of 1-ethyluracil, undetected in the infrared spectrum.

Registry No.—**1**, 936-70-9; **2**, 711-66-0; **3**, 15816-10-1; **4**, 15816-11-2; **5**, 15765-13-6; **6**, 15765-14-7; **7**, 15765-15-8; **8**, 15816-12-3; **9**, 15816-13-4; 1-(2-chloroethyl)-3-methyluracil, 15816-14-5; 1-(2-acetoxyethyl)-3-methyluracil, 15765-16-9; 1-vinyluracil, 15765-17-0; 1-vinyl-3-methyluracil, 15765-18-1.

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(33) A. Novacek, D. Hesoun, and J. Gut, *Collect. Czech. Chem. Commun.*, **30**, 1890 (1965).

(34) We are indebted to Dr. J. A. Montgomery for this sample.[24]