Evaporation of the solvent and recrystallization of the solid from methanol gave 3,5,5-triphenyl-2(5*H*)-furanone in 90% yield: mp 152–153°; ir (KBr) 1750 cm^{-1}; NMR ($CDCl_3$) δ 7.98 (s, 1 H), 7.31 (m, 15 H); uv (95% ethanol) 265 and 275 nm (ε 18,200 and 16,800); *m/e* (70 eV) 312 (M^+).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.28; H, 5.05.

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Registry No.—1, 13005-36-2; 2 (R_1 = R_2 = Ph), 36930-94-6; 4′-methoxybenzoin, 4254-17-5; diphenylacetaldehyde, 947-91-1.

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Preparation of 2,5-Diamino-4,6-dichloropyrimidine[1]

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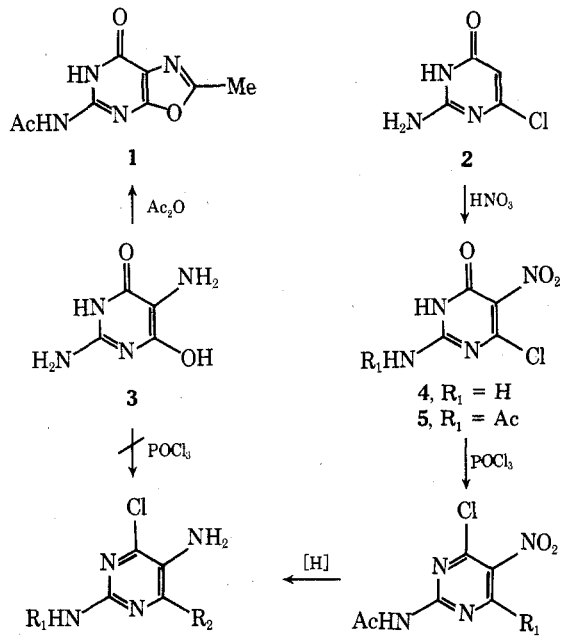
The projected routes for the synthesis of some condensed pyrimidine ring systems used 2,5-diamino-4,6-dichloropyrimidine (**7**) as a key intermediate. Previously, this compound was obtained in two steps from 2,4,6-trichloro-5-nitropyrimidine, which was prepared by the chlorodehydroxylation of 5-nitrobarbituric acid.[2] In one experiment in our laboratories, treatment of 5-nitrobarbituric acid with $POCl_3$ gave a 4% yield of the desired product. In two other experiments, the addition of *N,N*-dimethylaniline to the $POCl_3$ mixture gave a violet, exothermic reaction (induction period) resulting in the loss of the reactants. For this reason another route for the preparation of **7** was sought.

The chlorination of **3** with $POCl_3$ to give **7** directly was unsuccessful, apparently because of degradation of the ring system. To block the amino groups, **3** was treated with hot Ac_2O, but this reaction resulted in the formation of the oxooxazolopyrimidine **1**. Chlorination of **1** gave a mixture of products containing one to four chlorine atoms (mass spectrum), and the investigation of this approach was terminated.

In the successful route, the 5-nitropyrimidine **4**[3] was prepared from **2**[4] and purified by conversion to its acetylamino derivative **5**. Treatment of **5** with refluxing $POCl_3$ gave the dichloropyrimidine **9**. In some runs this product was contaminated with a minor impurity, presumably the corresponding 2-aminopyrimidine resulting from deacetylation of **9**. This impurity was reconverted to **9** by recrystallization of the sample from Ac_2O. In one experiment, the product was contaminated with **5**, apparently resulting from hydrolysis of **9** during the work-up of the acidic reaction medium. Treatment of **9** with an equimolar amount of benzyl carbazate at room temperature gave a 37% yield of **10**. Since it is known that the chloro group of 2,4-diamino-6-chloro-5-nitropyrimidine is replaced by amines under mild conditions,[5] the reaction of **9** with 2 equiv of the carbazate was not attempted.



Hydrogenation of **9** in the presence of Raney nickel gave the 5-amino compound **6**. Replacement of one chloro group and removal of the 2-acetyl group was accomplished by treatment of **6** with ethanolic hydrazine at room temperature to give **8**. In some preparations of **6**, this product was contaminated with the corresponding deacetylated compound **7**. Treatment of either **6** or a mixture of **6** and **7** with ethanolic HCl hydrolyzed the 2-acetyl group to give **7**. The reason for the considerable difference between the melting points of **7** and that previously prepared[2] is unknown. The use of **7** in the preparation of a pteridine has been reported.[6]

Experimental Section[7]

***N*-(6,7-Dihydro-2-methyl-7-oxooxazolo[5,4-*d*]pyrimidin-2-yl)acetamide (1).** A mixture of **3** hemisulfate (6.0 g, 31 mmol) and Ac_2O (60 ml) was heated with stirring at 100° for 3.5 hr. The solid that deposited from the resulting solution was collected by filtration and washed with Et_2O: yield 3.3 g (50%); mp 294°. For analyses a portion of this sample (0.5 g) was recrystallized from H_2O yield, 0.3 g; mp 303°; λ_{max} (ε × 10^{-3}) pH 7 253 nm (15.0), 279 (11.3); $\bar{\nu}_{max}$ 1670 cm^{-1}.

Anal. Calcd for $C_8H_8N_4O_3$: C, 46.16; H, 3.88; N, 26.92. Found: C, 46.30; H, 4.27; N, 27.39.

***N*-(6-Chloro-3,4-dihydro-5-nitro-4-oxopyrimidin-2-yl)acetamide (5).** Solid **2** (10 g, 69 mmol) was added with stirring at 17.5° to 140 ml of of a 1:1 mixture of concentrated sulfuric acid–nitric acid (*d* 1.49–1.50). The solid dissolved in several minutes and the temperature rose to 35°. After 50 min the solution was poured with stirring into crushed ice (500 g). The solid that deposited was collected by filtration, washed with water, and dried in vacuo over P_2O_5. The resulting crude sample of **4**[3] was extracted with acetone (4 × 500 ml), and the combined extract was evaporated to dryness in vacuo. The resulting solid was suspended in acetic anhydride (100 ml) containing 2 drops of concentrated sulfuric acid, and the whole was heated in a preheated oil bath at 90° for 30 min. The resulting hot solution was filtered, and the filtrate was cooled to deposit **5**: yield 8.7 g; mp 260° dec (Kofler Heizbank); λ_{max} (ε × 10^{-3}) pH 7 242 nm (10.2), 278 sh (3.72), 356 (2.02); $\bar{\nu}_{max}$ 1680 cm^{-1}.

Anal. Calcd for $C_6H_5ClN_4O_4$: C, 30.95; H, 2.15; Cl, 15.27; N, 24.10. Found: C, 30.71; H, 2.29; Cl, 14.83; N, 23.73.

Concentration of the acetic anhydride filtrate to a volume of about 15 ml deposited a second crop of product: yield, 1.4 g; mp 260° dec.

***N*-(5-Amino-4,6-dichloropyrimidin-2-yl)acetamide (6).** A solution of **9** (7.2 g, 29 mmol) in a mixture of DMAC (40 ml) and EtOH (750 ml) was hydrogenated in the presence of Raney nickel (7 g wet, washed with H_2O and EtOH) at room temperature and atmospheric pressure. The theoretical amount of H_2 was absorbed within 5 hr. The reaction mixture was filtered (Celite) under N_2, and the colored filtrate was evaporated in vacuo to give a gummy solid. This residue was triturated with Et_2O, and the brown solid was collected by filtration and dried in vacuo over P_2O_5 for 4 hr: yield 2.8 g (44%); mp 135–138° dec; λ_{max} ($\epsilon \times 10^{-3}$) pH 7 263 nm (12.1), 318 (4.79); $\bar{\nu}_{max}$ 1665 cm^{-1}.

Anal. Calcd for $C_6H_6Cl_2N_4O$: C, 32.60; H, 2.74; N, 25.34. Found: C, 32.37; H, 2.94; N, 25.09.

The Et_2O wash was evaporated to dryness to give a yellow solid, yield 3.9 g. TLC (silica gel, 9:1 $CHCl_3$–MeOH) indicated that this residue was a mixture of **6** and the corresponding deacetylated compound, **7** (see below).

2,5-Diamino-4,6-dichloropyrimidine (7). The mixture of **6** and **7** (3.9 g) obtained in the preparation of **6** was suspended in 6 *M* ethanolic HCl (40 ml) and stirred at room temperature for 3 hr. The solid was collected by filtration, washed with Et_2O, and dried in vacuo over P_2O_5: yield, 3.0 g; mp >264°.

Anal. Calcd for $C_4H_4Cl_2N_4 \cdot HCl \cdot 0.25C_2H_6O$: C, 23.81; H, 2.36; N, 24.68. Found: C, 23.86; H, 2.63; N, 24.80.

An additional amount of **7** (0.2 g) was obtained from the ethanol filtrate.

A portion of the first crop (1.0 g) was suspended in H_2O (25 ml), and the pH was adjusted to 7 by the addition of solid $NaHCO_3$. After stirring for 10 min, the mixture was heated at 50° for 15 min. After cooling the cream-colored solid was collected by filtration, washed with water, and dried in vacuo over P_2O_5: yield 0.6 g; mp 188–191° dec (lit.[2] mp 260–261°). In some samples decomposition occurred before melting unless the melting point was taken rapidly: λ_{max} ($\epsilon \times 10^{-3}$) pH 7 245 nm (13.0), 341 (4.84); $\bar{\nu}_{max}$ 1645 cm^{-1}; M^+ *m/e* 178, 180, 182.

Anal. Calcd for $C_4H_4Cl_2N_4$: C, 26.84; H, 2.25; N, 31.30. Found: C, 26.94; H, 2.49; N, 31.56.

2,5-Diamino-4-chloro-6-hydrazinopyrimidine (8). A suspension of **6** (1.0 g, 4.5 mmol) in EtOH (20 ml) containing anhydrous hydrazine (1.2 ml) was stirred at room temperature for 72 hr. The brown solid was collected by filtration, washed with Et_2O and then H_2O, and dried in vacuo over P_2O_5: yield 0.47 g (53%); mp >260°; λ_{max} ($\epsilon \times 10^{-3}$) pH 7 305 nm (5.05); $\bar{\nu}_{max}$ 1620 cm^{-1}.

Anal. Calcd for $C_4H_7ClN_6 \cdot H_2O$: C, 24.94; H, 4.71; N, 43.63. Found: C, 24.57; H, 4.36; N, 43.58.

An additional amount of crude **8** (0.28 g) was obtained from the water wash.

***N*-(4,6-Dichloro-5-nitropyrimidin-2-yl)acetamide (9).** A mixture of **5** (10.0 g, 43 mmol) and $POCl_3$ (200 ml) was refluxed for 4 hr. The resulting solution was concentrated under reduced pressure to a smaller volume (50 ml) and poured with vigorous stirring into an ice–H_2O mixture (1000 ml). The brown solid that precipitated was collected by filtration, washed with water (1000 ml), and dried in vacuo over P_2O_5: yield 7.3 g (67%); mp 206–207° dec. Although this material analyzed correctly for **9**, the melting point was increased by recrystallization of a sample (0.5 g) from hot Ac_2O: yield 0.25 g; mp 224°. This sample was homogeneous on TLC (silica gel, EtOAc, R_f 0.9) except for a spot at the origin: λ_{max} ($\epsilon \times 10^{-3}$) pH 7 240 nm (13.0), 247 sh (12.9), 275 sh (7.57), 340 br sh (0.95); $\bar{\nu}_{max}$ 1705 cm^{-1}; M^+ *m/e* 250, 252, 254.

Anal. Calcd for $C_6H_4Cl_2N_4O_3$: C, 28.71; H, 1.61; N, 22.32. Found: C, 28.88; H, 1.63; N, 22.48.

Benzyl 3-(2-Acetylamino-4-chloro-5-nitropyrimidin-6-yl)carbazate (10). A suspension of **9** (1.0 g, 4.0 mmol) in dioxane (40 ml) containing benzyl carbazate (0.68 g, 4.1 mmol) was stirred at room temperature for 60 hr. The solid was collected by filtration, washed sparingly with Et_2O, and dried in vacuo over P_2O_5 to give the dioxanate complex of **10**: yield 0.69 g (37%); mp 185–186° dec; λ_{max} ($\epsilon \times 10^{-3}$) pH 7 235 nm sh (10.8), 341 (11.1); $\bar{\nu}_{max}$ 1735 cm^{-1}.

Anal. Calcd for $C_{14}H_{13}ClN_6O_5 \cdot C_4H_8O_2$: C, 46.11; H, 4.51; N, 17.93. Found: C, 46.05; H, 4.84; N, 17.80.

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Registry No.—**1**, 56145-01-8; **2**, 1194-21-4; **3**, 40769-69-5; **5**, 51471-45-5; **6**, 56145-02-9; **7**, 55583-59-0; **7** HCl, 56145-03-0; **8**, 56227-23-7; **9**, 56145-04-1; **10** dioxane, 56145-06-3; acetic anhydride, 108-24-7; hydrazine, 302-01-2; benzyl carbazate, 5331-43-1.

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1,3-Bridged Aromatic Systems. XIV. The Effect of Configuration on the Course of Reactions of Alcohols with Thionyl Chloride and with Phosgene

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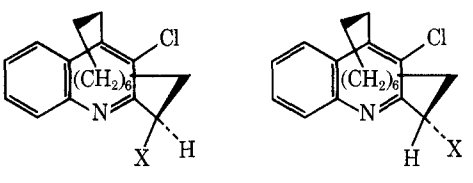
Continuing studies[1] of the chemistry of anti chloride **2b** and anti bromide **2c** have been inhibited by their lack of availability. While the syn bromide **1c** is readily available[2] by bromination of **1a** with *N*-bromosuccinimide, the anti chloride and bromide have only been obtained as by-products from reactions of the *N*-oxide of **1a** with acid halides.[1,3,4,5]



1 **2**

a, X = H
b, X = Cl
c, X = Br
d, X = OH

We have now observed that the anti chloride **2b** can be obtained conveniently and in high yield from the readily available anti alcohol **2d** by reaction with thionyl chloride in hot benzene. The reaction is stereoselective and occurs with complete retention of configuration.

Similar results were obtained with thionyl bromide; the yield of pure anti bromide **2c** was >67% and no syn bromide, which would be formed if inversion occurred at the benzylic carbon atom,[6] was detected.

By contrast, reaction of the corresponding syn alcohol **1d** with thionyl chloride in hot benzene did not lead to the syn