treatment and acidification), 4.99 equivalents per mole compound.

**Tetra-*O*-acetyl-α-D-glucopyranosyl Bromide from 2,3,4,6-Tetra-*O*-acetyl-1-*O*-mesitoyl-α-D-glucopyranose (X).**—2,3,4,6-Tetra-*O*-acetyl-1-*O*-mesitoyl-α-D-glucopyranose (200 mg.) was dissolved in methylene chloride (1.0 ml.) and 0.5 ml. of hydrogen bromide–acetic acid (32% w./w. HBr) added to the solution. After two hours at room temperature the mixture was diluted with a mixture of methylene chloride (15 ml.) and water and the organic layer washed successively with water and aqueous sodium bicarbonate. Moisture was removed with sodium sulfate, the solution concentrated *in vacuo* and the product crystallized from ether–pentane. The fine needles (148 mg., 84%) melted at 88–89° either alone or in admixture with authentic tetra-*O*-acetyl-α-D-glucopyranosyl bromide.

**Acknowledgment.**—Analyses were carried out by the Institutes' Microanalytical Laboratory under the direction of Dr. W. C. Alford.

BETHESDA 14, MARYLAND

---

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Pteridines. XIV.[1] Further Studies on a New Approach to Pteridine Synthesis[2]

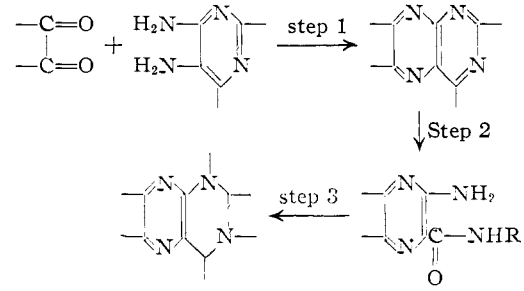
BY E. C. TAYLOR, JR.,[3] ROBERT B. GARLAND AND CHARLES F. HOWELL

RECEIVED MAY 25, 1955

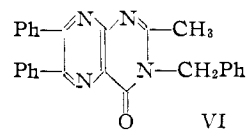
A number of additional cyclizations of 3-aminopyrazinamides and -thiopyrazinamides to pteridines have been carried out, and serve to illustrate further the scope and limitations of this new synthetic approach.

The conventional approach to pteridine synthesis involving the condensation of a 4,5-diaminopyrimidine with an α,β-dicarbonyl compound, an α-halo carbonyl compound, an α-keto alcohol or related derivatives of such intermediates, suffers from a number of disadvantages which are due in large part to limitations encountered in the synthesis of the requisite 4,5-diaminopyrimidines. The number of pteridines variously substituted in the pyrimidine portion of the ring, which are available *via* this approach, is thus severely restricted. The shortcomings of the conventional synthetic approach cannot be adequately compensated for by subsequent alterations of the resulting pteridine, since the latter, as a class, are particularly unsuited for substitution or displacement reactions, and desired substituent groups are best introduced before ring closure.[4,5]

A new approach to pteridine synthesis has been described recently[6] which retains the convenience and versatility of the conventional condensation reaction of a 4,5-diaminopyrimidine with a dicarbonyl reagent with regard to the placement of substituents in the pyrazine ring of the final pteridines, but whose special feature is the varied manner in which the pyrimidine ring may be constructed. The method consists of (a) the synthesis, by the conventional procedure, of a 4-hydroxy- or 2,4-dihydroxypteridine, in which the pyrazine ring carries the substituents desired in the final product; (2) cleavage of the pyrimidine portion of this pteridine, usually by hydrolysis or aminolysis, to give a 3-aminopyrazinamide or a derivative thereof; and (3) ring reclosure of the pyrazinamide to the desired pteridine. The present paper illustrates step 3 with a number of additional cyclization procedures.




The reaction of 3-amino-5,6-diphenylpyrazinamide (I) and 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II) with benzoyl chloride in the absence of a solvent led to the formation of 2,6,7-triphenyl-4(3*H*)-pteridinone (III) and 3-benzyl-2,6,7-triphenyl-4(3*H*)-pteridinone (IV), respectively. Attempts to carry out analogous cyclizations with acetyl chloride or acetic anhydride were not successful, however; the only product isolated in each case was the intermediate 3-acetylamino-5,6-diphenylpyrazinamide (V). Attempts to cyclize these pyrazinamides were likewise unsuccessful; 3-acetylamino-N-benzyl-5,6-diphenylpyrazinamide (V, R = $-CH_2Ph$) was unaffected by ammonia in ethanol or by fusion *in vacuo*, and gave 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II) on treatment with sodium ethoxide in ethanol. It is probable that, in the latter instance, the desired 2-methyl-3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone (VI) was



VI

formed initially but underwent immediate alkaline ring cleavage to the aminopyrazinamide II. This view is substantiated by the observation that 2,6,7-triphenyl-3-benzyl-4(3*H*)-pteridinone (IV) was converted smoothly to II by sodium ethoxide in eth-

(1) For the preceding paper in this series, see E. C. Taylor, Jr., H. M. Loux, E. A. Falco and G. H. Hitchings, THIS JOURNAL, **77**, 2243 (1955).

(2) Abstracted from theses presented by R. B. G. and C. F. H. to the University of Illinois in partial fulfillment for the degree of Bachelor of Science in Chemistry.

(3) Frick Chemical Laboratory, Princeton University, Princeton, N. J.

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

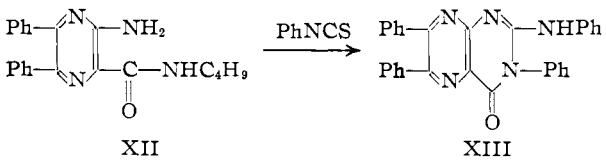
(5) E. C. Taylor, Jr., THIS JOURNAL, **74**, 2380 (1952).

(6) E. C. Taylor, Jr., J. A. Carbon and D. R. Hoff, *ibid.*, **75**, 1904 (1953).

anol under similar conditions. These examples serve to illustrate further the extreme lability toward alkali of pteridines lacking an enolizable grouping in the 2-position and unable to form a simple anion.[5]

When I and II were treated with phenyl isocyanate in pyridine solution for one hour, the corresponding 3-(3-phenylureido)-5,6-diphenylpyrazinamides VII and VIII were obtained. Treatment of VII, VIII or II with polyphosphoric acid gave 3-amino-5,6-diphenylpyrazinamide (I), probably *via* 2-cyano-3-amino-5,6-diphenylpyrazine, although with VII, concomitant cyclization took place to give 3,6,7-triphenyl-2,4(1*H*,3*H*)-pteridinedione (IX). The latter pteridinedione was the exclusive product of the reaction of both I and II with phenyl isocyanate in pyridine solution for three days. In the latter case, the N-benzyl group was lost during the cyclization. Attempts to cyclize VIII with phosphorus pentoxide in benzene or with alcoholic ammonia were unsuccessful.

The reaction of I with phenyl isothiocyanate in pyridine solution proceeded similarly; the product isolated after a reaction time of one hour was 3-(3-phenylthioureido)-5,6-diphenylpyrazinamide (X) and the product isolated after a reaction time of three days was 2-mercapto-3,6,7-triphenyl-4(3*H*)-pteridinone (XI). However, the reaction of 3-amino-N-(*n*-butyl)-5,6-diphenylpyrazinamide (XII) with phenyl isothiocyanate took an unexpected course, for the only product isolated from the reaction was 2-anilino-3,6,7-triphenyl-4(3*H*)-pteridinone (XIII).




XII XIII

The reaction of I and II with isopropyl isothiocyanate in pyridine solution gave the corresponding 3-(3-isopropylthioureido)-5,6-diphenylpyrazinamides (XIV and XV), but no cyclization was observed even on prolonged heating of the reaction mixtures. However, cyclization was effected with sodium ethoxide. XIV was converted into a mixture of 2-mercapto-3-isopropyl-6,7-diphenyl-4(3*H*)-pteridinone (XVI) and 2-isopropylamino-6,7-diphenyl-4(3*H*)-pteridinone (XVII), while XV was converted into 2-isopropylamino-3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone (XVIII). XVI was not isolated from the latter cyclization.

A number of cyclization reactions have been reported[6] with the thioamide XIX, prepared by the action of phosphorus pentasulfide in pyridine solution on the corresponding amide I. Several additional cyclizations of this intermediate have now been carried out. Treatment of XIX with acetic anhydride, or with acetyl chloride in benzene or with benzoyl chloride in benzene, failed to give a product which could be characterized. However, treatment of XIX with benzoyl chloride in the absence of a solvent gave 2,6,7-triphenyl-4(3*H*)-pteridinethione (XX). The reaction of XIX with phenyl isocyanate in pyridine solution either for one hour or for three days gave a high melting (369–370°), insoluble yellow compound of empirical formula $C_{47}H_{33}N_9O$, to which, on the basis of physical and chemical properties and microanalytical values, the tentative structures XXIa or XXIb are assigned. The reaction of XIX with phenyl isothiocyanate in pyridine solution proceeded as expected to give 2-anilino-6,7-diphenyl-4(3*H*)-pteridinethione (XXII).

Since the pyrazine intermediates required for the preceding cyclization experiments are all obtainable by ring cleavage of readily available pteridines, the approach to pteridine synthesis involving ring reclosure of appropriately substituted pyrazine intermediates with a properly chosen reagent, as exemplified by the preceding examples, offers considerable promise as a general and versatile method for the synthesis of pteridines generally unobtainable by any other known synthetic route.

## Experimental[7]

**2,6,7-Triphenyl-4(3*H*)-pteridinone (III).**—A mixture of 1.509 g. of 3-amino-5,6-diphenylpyrazinamide (I) and 10 ml. of benzoyl chloride was heated under reflux for four hours, cooled and diluted with 250 ml. of petroleum ether. The orange crystals which separated (1.179 g., 60%) were collected by filtration and recrystallized first from methylene chloride–petroleum ether and then from aqueous dimethylformamide to give white needles, m.p. 290°.

*Anal.* Calcd. for $C_{24}H_{16}N_4O$: C, 76.6; H, 4.3; N, 14.9. Found: C, 76.6; H, 4.2; N, 14.9.

**3-Benzyl-2,6,7-triphenyl-4(3*H*)-pteridinone (IV).**—A mixture of 0.519 g. of 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II) and 5 ml. of benzoyl chloride was heated under reflux for four hours, cooled and diluted with 100 ml. of petroleum ether. The resulting mixture was allowed to stand for several days with occasional stirring until the tarry appearance of the precipitate had disappeared, and the collected solid was then recrystallized from chloroform–petroleum ether to give 0.458 g. (72%) of small white needles, m.p. 227.5–228.4°.

*Anal.* Calcd. for $C_{31}H_{22}N_4O$: C, 79.8; H, 4.7; N, 12.0. Found: C, 79.5; H, 4.6; N, 12.0.

**3-Acetylamino-5,6-diphenylpyrazinamide** (V, R = H).—A mixture of 0.5 g. of 3-amino-5,6-diphenylpyrazinamide (I) and 25 ml. of acetyl chloride was heated under reflux for four hours. Addition of 25 ml. of petroleum ether to the cooled reaction mixture precipitated a yellow, amorphous solid which was collected by filtration and washed thoroughly with petroleun ether. Recrystallization from chloroform–petroleum ether gave 0.36 g. (63%) of bright yellow platelets, m.p. 207–208°.

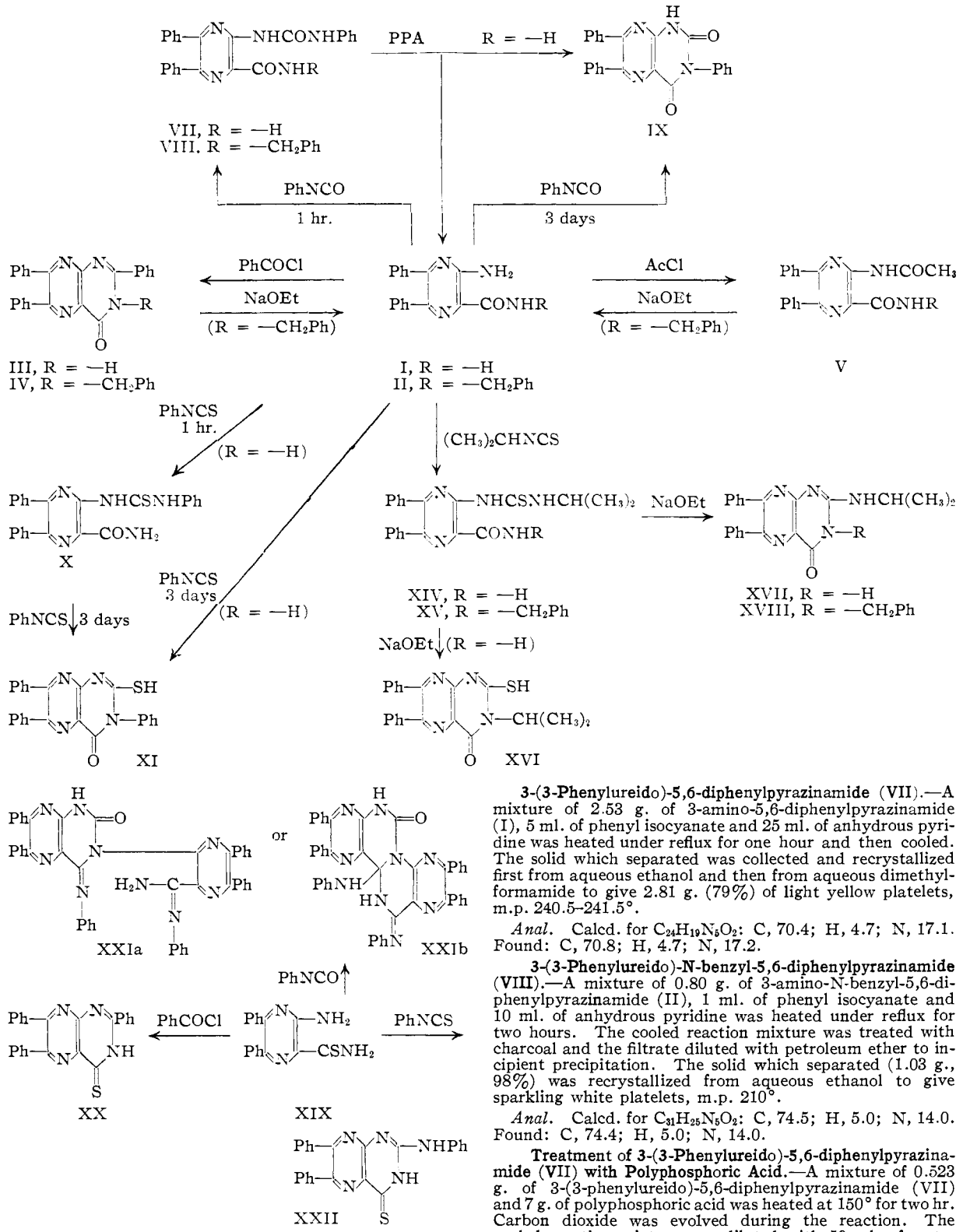
*Anal.* Calcd. for $C_{19}H_{16}N_4O_2$: C, 68.7; H, 4.8; N, 16.9. Found: C, 68.4; H, 4.6; N, 16.7.

**3-Acetylamino-N-benzyl-5,6-diphenylpyrazinamide** (V, R = $CH_2Ph$).—A mixture of 0.835 g. of 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II), 10 ml. of acetic anhydride and 10 ml. of acetonitrile was heated under reflux for four hours, and the resulting clear yellow solution was evaporated to dryness under reduced pressure. Ethanol was added to the residue and the solution again evaporated to dryness. Recrystallization of the residue from methylene chloride–petroleum ether gave 0.472 g. (51%) of tan crystals, m.p. 149–150°.

*Anal.* Calcd. for $C_{26}H_{22}N_4O_2$: C, 73.9; H, 5.3; N, 13.3. Found: C, 73.9; H, 5.4; N, 13.3.

**Reaction of 3-Acetylamino-N-benzyl-5,6-diphenylpyrazinamide with Sodium Ethoxide.**—To a solution of sodium ethoxide, prepared by dissolving 0.5 g. of sodium in 10 ml. of absolute ethanol, was added 0.613 g. of the above compound. The solution was heated under reflux for three hours and then poured into 50 ml. of water. The precipitated solid (0.503 g., 91% yield), m.p. 186–187°, was shown to be 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II) by a mixed melting point determination.

(7) Microanalyses were performed by Mrs. Lucy Chang, Mrs. Esther Fett and Mr. Joseph Nemeth. All melting points are corrected.




**Reaction of 3-Benzyl-2,6,7-triphenyl-4(3*H*)-pteridinone (IV) with Sodium Ethoxide.**—Treatment of IV with a solution of sodium ethoxide under the conditions described immediately above gave a 93% yield of 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II), m.p. 186–187°. A mixed melting point determination with an authentic sample showed no depression.

**3-(3-Phenylureido)-5,6-diphenylpyrazinamide (VII).**—A mixture of 2.53 g. of 3-amino-5,6-diphenylpyrazinamide (I), 5 ml. of phenyl isocyanate and 25 ml. of anhydrous pyridine was heated under reflux for one hour and then cooled. The solid which separated was collected and recrystallized first from aqueous ethanol and then from aqueous dimethylformamide to give 2.81 g. (79%) of light yellow platelets, m.p. 240.5–241.5°.

*Anal.* Calcd. for $C_{24}H_{19}N_5O_2$: C, 70.4; H, 4.7; N, 17.1. Found: C, 70.8; H, 4.7; N, 17.2.

**3-(3-Phenylureido)-N-benzyl-5,6-diphenylpyrazinamide (VIII).**—A mixture of 0.80 g. of 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II), 1 ml. of phenyl isocyanate and 10 ml. of anhydrous pyridine was heated under reflux for two hours. The cooled reaction mixture was treated with charcoal and the filtrate diluted with petroleum ether to incipient precipitation. The solid which separated (1.03 g., 98%) was recrystallized from aqueous ethanol to give sparkling white platelets, m.p. 210°.

*Anal.* Calcd. for $C_{31}H_{25}N_5O_2$: C, 74.5; H, 5.0; N, 14.0. Found: C, 74.4; H, 5.0; N, 14.0.

**Treatment of 3-(3-Phenylureido)-5,6-diphenylpyrazinamide (VII) with Polyphosphoric Acid.**—A mixture of 0.523 g. of 3-(3-phenylureido)-5,6-diphenylpyrazinamide (VII) and 7 g. of polyphosphoric acid was heated at 150° for two hr. Carbon dioxide was evolved during the reaction. The cooled reaction mixture was diluted with 50 ml. of water and the precipitated solid collected by filtration, dried and sublimed at 200° (2 mm.). The yellow sublimate, m.p. 204–205° (0.134 g., 36%), was shown to be 3-amino-5,6-diphenylpyrazinamide (I) by comparison with an authentic sample. The residue from the initial sublimation was then sublimed at 300° (0.2 mm.) to give a colorless solid, m.p. 327–328° dec. which was identified as 3,6,7-triphenyl-2,4-

(1*H*,3*H*)-pteridinedione (IX) by analysis and by independent synthesis (see below).

*Anal.* Calcd. for $C_{24}H_{16}N_4O_2$: C, 73.5; H, 4.1; N, 14.3. Found: C, 73.8; H, 4.1; N, 14.5.

In a similar manner, 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II) and polyphosphoric acid at 150° for 45 minutes gave 2-amino-5,6-diphenylpyrazinamide (I) in 52% yield, and 3-(3-phenylureido)-N-benzyl-5,6-diphenylpyrazinamide (VIII) yielded I in 63% yield.

**3,6,7-Triphenyl-2,4(1*H*,3*H*)-pteridinedione (IX). Method A.**—A mixture of 0.97 g. of 3-amino-5,6-diphenylpyrazinamide (I), 2 ml. of phenyl isocyanate and 10 ml. of pyridine was heated under reflux for three days. Dilution of the cooled reaction mixture with 40 ml. of methylene chloride and 250 ml. of petroleum ether precipitated a small amount of diphenylurea which had formed in the course of the reaction, and evaporation of the filtrate to dryness and recrystallization of the residue from aqueous dimethylformamide gave 0.418 g. (32%) of white needles, m.p. 327–328° dec., which were shown to be identical with the sample of IX prepared above by a mixture melting point determination and by comparison of infrared spectra.

**Method B.**—IX was formed in 51% yield by the reaction of 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II) with phenyl isocyanate in pyridine solution under similar conditions.

**3-(3-Phenylthioureido)-5,6-diphenylpyrazinamide (X).**—A mixture of 1.52 g. of 3-amino-5,6-diphenylpyrazinamide (I), 3 ml. of phenyl isothiocyanate and 15 ml. of pyridine was heated under reflux for one hour. Dilution of the cooled reaction mixture with 150 ml. of petroleum ether yielded 1.92 g. (87%) of a yellow solid which was recrystallized from aqueous dimethylformamide to give light yellow platelets, m.p. 233°.

*Anal.* Calcd. for $C_{24}H_{19}N_5SO$: C, 67.7; H, 4.5; N, 16.5. Found: C, 68.0; H, 4.8; N, 16.0.

**2-Mercapto-3,6,7-triphenyl-4(3*H*)-pteridinone (XI).**—A mixture of 1.67 g. of 3-amino-5,6-diphenylpyrazinamide (I), 3 ml. of phenyl isothiocyanate and 15 ml. of pyridine was heated under reflux for three days. The reaction mixture was cooled overnight and the solid which had separated was collected by filtration, washed well with petroleum ether and recrystallized from aqueous dimethylformamide to give 1.87 g. (80%) of fine yellow needles, m.p. 301–302°. The analytical sample was prepared by sublimation at 250° (1 mm.).

*Anal.* Calcd. for $C_{24}H_{16}N_4SO$: C, 70.6; H, 4.0; N, 13.7. Found: C, 70.6; H, 3.9; N, 13.8.

XI was formed in comparable yield by heating X with phenyl isothiocyanate under similar conditions.

**2-Anilino-3,6,7-triphenyl-4(3*H*)-pteridinone (XIII).**—A solution of 2.70 g. of 3-amino-N-(*n*-butyl)-5,6-diphenylpyrazinamide (XII), 3.5 ml. of phenyl isothiocyanate and 10 ml. of pyridine was heated under reflux for four days. The product was precipitated from the cooled reaction mixture by the addition of 20 ml. of methylene chloride followed by 100 ml. of petroleum ether, and was recrystallized from aqueous dimethylformamide to give 1.49 g. (42%) of pale yellow crystals, m.p. 323–324°.

*Anal.* Calcd. for $C_{30}H_{21}N_5O$: C, 77.1; H, 4.5; N, 15.0. Found: C, 76.7; H, 4.4; N, 15.1.

**The 3-(3-Isopropylthioureido)-5,6-diphenylpyrazinamide (XIV).**—A solution of 1.34 g. of 3-amino-5,6-diphenylpyrazinamide (I), 2 ml. of isopropyl isothiocyanate and 20 ml. of pyridine was heated under reflux for two days. The product was precipitated from the cooled reaction mixture by the addition of 25 ml. of chloroform followed by 100 ml. of petroleum ether and cooling the mixture at 0° overnight. The collected solid was recrystallized from methylene chloride–cyclohexane to give 1.05 g. (58%) of white platelets, m.p. 251–252°.

*Anal.* Calcd. for $C_{21}H_{21}N_5OS$: C, 64.4; H, 5.4; N, 17.9. Found: C, 64.8; H, 5.3; N, 17.6.

**3-(3-Isopropylthioureido)-N-benzyl-5,6-diphenylpyrazinamide (XV).**—A mixture of 1.04 g. of 3-amino-N-benzyl-5,6-diphenylpyrazinamide (II), 1.2 ml. of isopropyl isothiocyanate and 15 ml. of pyridine was heated under reflux for two days and then poured on 200 g. of ice. The resulting solid mass which separated was collected by filtration and recrystallized from 70% acetic acid to yield 0.7 g. (53%) of pale yellow crystals, m.p. 170°.

*Anal.* Calcd. for $C_{28}H_{27}N_5OS$: C, 69.8; H, 5.6; N, 14.6. Found: C, 69.7; H, 5.5; N, 14.6.

**2-Mercapto-3-isopropyl-6,7-diphenyl-4(3*H*)-pteridinone (XVI).**—To a solution of sodium ethoxide prepared by the addition of 1 g. of sodium to 25 ml. of absolute ethanol was added 1.24 g. of 3-(3-isopropylthioureido)-5,6-diphenylpyrazinamide (XIV) and the mixture heated under reflux for six hours. It was then poured into 100 ml. of water and the orange precipitate which separated was removed by filtration, digested with dilute hydrochloric acid and the free pteridinone recrystallized from aqueous ethanol to give 0.174 g. (15%) of light yellow needles, m.p. 270°.

*Anal.* Calcd. for $C_{21}H_{18}N_4OS$: C, 67.4; H, 4.8; N, 15.0. Found: C, 67.2; H, 4.5; N, 14.7.

**2-Isopropylamino-6,7-diphenyl-4(3*H*)-pteridinone (XVII).**—The above filtrate was acidified with concentrated hydrochloric acid. Hydrogen sulfide was evolved and a yellow solid separated which was collected by filtration, washed well with water and recrystallized from aqueous ethanol to give 0.72 g. (64%) of bright lemon-yellow platelets, m.p. 324–325°. The analytical sample was prepared by sublimation at 250° (1 mm.).

*Anal.* Calcd. for $C_{21}H_{19}N_5O$: C, 70.6; H, 5.4; N, 19.6. Found: C, 70.4; H, 5.2; N, 19.3.

**2-Isopropylamino-3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone (XVIII).**—To a solution of sodium ethoxide, prepared by adding 0.1 g. of sodium to 5 ml. of absolute ethanol, was added 0.390 g. of N-benzyl-3-(3-isopropylthioureido)-5,6-diphenylpyrazinamide (XV). The solution was heated under reflux for three hours and then poured into 50 ml. of water. The orange solid which separated was collected by filtration and recrystallized from aqueous dimethylformamide to give 0.30 g. (83%) of sparkling yellow crystals, m.p. dec. 305–307°.

*Anal.* Calcd. for $C_{28}H_{25}N_5O$: C, 75.1; H, 5.6; N, 15.6. Found: C, 75.1; H, 5.8; N, 15.6.

**2,6,7-Triphenyl-4(3*H*)-pteridinethione (XX).**—A mixture of 1.1 g. of 3-amino-5,6-diphenylthiopyrazinamide (XIX) and 10 ml. of benzoyl chloride was heated under reflux for 1.5 hours. It was then cooled, diluted with 50 ml. of ethanol and the mixture again heated under reflux for one hour. It was then evaporated to dryness under reduced pressure and the residue suspended in hot ethanol and filtered. The insoluble residue was sublimed to give a yellow crystalline solid, m.p. 323–324°.

*Anal.* Calcd. for $C_{24}H_{16}N_4S$: C, 73.4; H, 4.1; N, 14.3. Found: C, 73.0; H, 4.1; N, 14.9.

**Reaction of 3-Amino-5,6-diphenylthiopyrazinamide (XIX) with Phenyl Isocyanate.**—A mixture of 1.23 g. of 3-amino-5,6-diphenylthiopyrazinamide (XIX), 3.4 ml. of phenyl isocyanate and 10 ml. of pyridine was heated under reflux for two hours. A yellow solid started to separate from the solution after a period of one hour. The cooled reaction mixture was then diluted with 180 ml. of petroleum ether and the precipitated solid collected by filtration and recrystallized from aqueous dimethylformamide to give 2.06 g. (70%) of fine yellow needles, m.p. 369–370°.

*Anal.* Calcd. for $C_{47}H_{33}N_9O$: C, 76.3; H, 4.5; N, 17.0. Found: C, 76.2; H, 4.4; N, 17.2.

The same product (XXIa or XXIb) was obtained when the reaction mixture was heated under reflux for three days and then worked up as described above. The product was recovered in 93% yield after refluxing with concentrated hydrochloric acid for 43 hr.

**2-Anilino-6,7-diphenyl-4(3*H*)-pteridinethione (XXII).**—A mixture of 1.04 g. of 3-amino-5,6-diphenylthiopyrazinamide (XIX), 2 ml. of phenyl isothiocyanate and 10 ml. of pyridine was heated under reflux for 36 hours and then diluted with 150 ml. of hot petroleum ether. Standing caused the separation of (1) large colorless needles, m.p. 72–157°, obtained in only very small quantity and not investigated further; (2) fine yellow needles; and (3) cushions of orange prisms. Recrystallization of fractions (2) and (3) from pyridine–petroleum ether gave long yellow needles, m.p. 261–262°, which were shown to be identical by a mixed melting point determination; total yield, 1.15 g. (84%).

*Anal.* Calcd. for $C_{24}H_{17}N_5S$: C, 70.7; H, 4.2; N, 17.2. Found: C, 70.8; H, 4.3; N, 17.3.

PRINCETON, NEW JERSEY