50 cc. of *p*-dioxane. This solution was added dropwise to a mixture of 7.4 g. of ethyl *p*-aminobenzoate and 3.8 g. of $NaHCO_3$. The mixture was then refluxed with stirring for 3 hours. At the end of this time the solution was filtered hot to remove the excess of $NaHCO_3$. Upon cooling, crystals separated which were purified by subsequent recrystallization from dioxane; yield 8.1 g. (75.8%), m.p. 229°.

Anal. Calcd. for $C_{27}H_{25}N_5O_4$: C, 67.1; H, 5.5; N, 14.57. Found: C, 67.03; H, 5.22; N, 14.8.

2-Phenyl-4,6-dihydrazine-*s*-triazine.—To a solution of 150 cc. of acetonitrile containing 22.5 g. of 2-phenyl-4,6-dichloro-*s*-triazine, a solution of 100 cc. of ethanol containing 15 g. of hydrazine and 50 cc. of water was added. The mixture was heated for about 30 minutes. After cooling, the precipitate was collected and washed with hot water, ethanol and ether; yield 21 g. (97%), m.p. 182–184°.

Anal. Calcd. for $C_9H_{11}N_7$: C, 49.9; H, 5.05; N, 45.05. Found: C, 49.9; H, 4.99; N, 44.76.

2-Methyl-4,6-bis-(diphenylamino)-*s*-triazine.—A solution of 300 cc. of 1,4-dioxane containing 16.3 g. of 2-methyl-4,6-dichloro-*s*-triazine and 67.6 g. of diphenylamine was heated under reflux for about 5 hours. The reaction mixture was allowed to stand at room temperature overnight. After filtration, about 200 cc. of dioxane was distilled off. The remaining solution was diluted with 100 cc. of chloroform. This resulting solution was washed five times with 100-cc. portions of water, then dried over $CaCl_2$. After addition of ligroin (60–70°), precipitation occurred. The solid material was purified by recrystallization from isopropyl alcohol; yield 40.5 g. (94.5%), m.p. 209–210°.

Anal. Calcd. for $C_{28}H_{23}N_5$: C, 78.2; H, 5.36; N, 16.3. Found: C, 78.14; H, 5.30; N, 16.32.

2-Bromomethyl-4,6-bis-(diphenylamino)-*s*-triazine.—A solution of 100 cc. of carbon tetrachloride containing 10.75 g. of 2-methyl-4,6-bis-N-phenylanilino-*s*-triazine, 0.05 g. of benzoyl peroxide and 5 g. of N-bromo-succinimide was heated under reflux with mechanical stirring for 2 hours. During this time the mixture was irradiated with ultraviolet light. During reaction the succinimide precipitated from solution. After cessation of reaction the succinimide was separated by filtration of the hot solution, washing with carbon tetrachloride and the washings added to the original filtrate. After evaporation of the carbon tetrachloride the remainder was extracted with ligroin. Recrystallization from ligroin afforded the pure 2-bromomethyl-4,6-bis-(diphenylamino)-*s*-triazine; yield 10.5 g. (82%), m.p. 146–148°.

Anal. Calcd. for $C_{28}H_{22}N_5Br$: C, 66.15; H, 4.34; N, 13.80; Br, 15.71. Found: C, 66.46; H, 4.36; N, 13.81; Br., 15.43.

2-Dicarboethoxy-phenylmethyl-4,6-dimethoxy-*s*-triazine.—Sodium (6 g.) was dissolved in 100 cc. of absolute ethanol. The ethanol then was distilled off and the remaining sodium ethoxide pulverized by vigorous stirring. After cooling, 58.5 g. of diethyl phenylmalonate dissolved in 50 g. of diethyl carbonate was added. Stirring was allowed to continue at room temperature until all sodium ethoxide had reacted. The ethanol formed by this reaction was removed by distillation under diminished pressure. A solution of 50 g. of diethyl carbonate containing 50 g. of 2-chloro-4,6-dimethoxy-*s*-triazine was added and the mixture was heated at 100–110° for 8 hours. After standing overnight at room temperature a solution of 2 cc. of glacial acetic acid in 200 cc. of distilled water was then added. The product crystallized from this solution was collected and washed with water, alcohol and ether; yield 61 g. (65%). After recrystallization from ethanol the material melted at 112–113°.

Anal. Calcd. for $C_{18}H_{21}O_6N_3$: C, 57.7; H, 5.6; N, 11.2. Found: C, 57.49; H, 5.62; N, 11.23.

Infrared Spectra. Apparatus.—The infrared investigations were carried out with a Baird associates model B double beam spectrophotometer equipped with a sodium chloride prism. The instrument was calibrated with a polystyrene film to within ±0.05 μ.

Technique.—Mallinckrodt reagent grade carbon tetrachloride and carbon disulfide were used as solvents for the triazine derivatives 2 through 11. Each sample contained 20 mg. per ml. which seemed to be the maximum concentration that could be obtained with this set of derivatives. This limited concentration required that a 0.4-mm. cell be used in order to obtain enough detail in the spectra between 8 and 11 μ. Figure 1,1 shows the absorption bands due to the solvents. In all of the solution spectra carbon tetrachloride was used to 7.6 μ and then carbon disulfide to 15 μ. In the regions where the solvents absorb strongly in the 0.4-mm. cell the spectra were re-run in a 0.07-mm. cell at the same concentration.

The triazine derivatives A through I were not soluble in these solvents and their spectra were recorded as solids in potassium bromide wafers. Between 1 and 1.5 mg. of ground sample was mixed with 200 mg. of infrared quality potassium bromide powder on a Wig-l-Bug[12] and pressed at 10,000 p.s.i. for four minutes. The wafers were 0.4 mm. thick and a 25% transmission screen was used in the reference beam.

(12) Spex Industries, Scotch Plains, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Stereospecific Lithium Aluminum Hydride Reduction of 2,3-Dimethylquinoxaline and Related Triazanaphthalenes[1]

BY ROY C. DESELMS[2] AND HARRY S. MOSHER

RECEIVED DECEMBER 9, 1959

The lithium aluminum hydride reduction of 2,3-dimethylquinoxaline gives the *cis*-tetrahydro derivative contrary to the previous literature. This is a stereospecific reduction since the reagent does not isomerize the *trans* compound to the *cis*. This reduction is applied to 2,3-dimethyl-1,4,5-triazanaphthalene and 2,3-dimethyl-1,4,6-triazanaphthalene to give the corresponding tetrahydro derivatives which are presumed to have the *cis* configuration. The ultraviolet and infrared spectra of these compounds are reported and discussed.

During a recent study[1] of the synthesis of certain analogs of tetrahydropteroic acid, it became desirable to investigate the selective reduction of some related polyazanaphthalenes to the corresponding tetrahydro derivatives. The pyrazine ring in other fused heterocyclic systems has been preferentially reduced[3,4] and it seemed likely that this could be extended to the pyridopyrazines under study.

It was reported by Bohlmann[5] that the lithium aluminum hydride reduction of 2,3-dimethylquinoxaline gave a product, m. p. 102–103°, which he concluded was the same as the compound of the

(1) Abstracted in part from the Ph.D. Dissertation of Roy C. De Selms, Stanford Univ., 1959.

(2) Research Laboratories, Eastman Kodak Co., Rochester 4, N. Y.

(3) E. C. Taylor and W. R. Sherman, THIS JOURNAL, **81**, 2464 (1959).

(4) A. Albert, *Quart. Revs.*, **6**, 197 (1952).

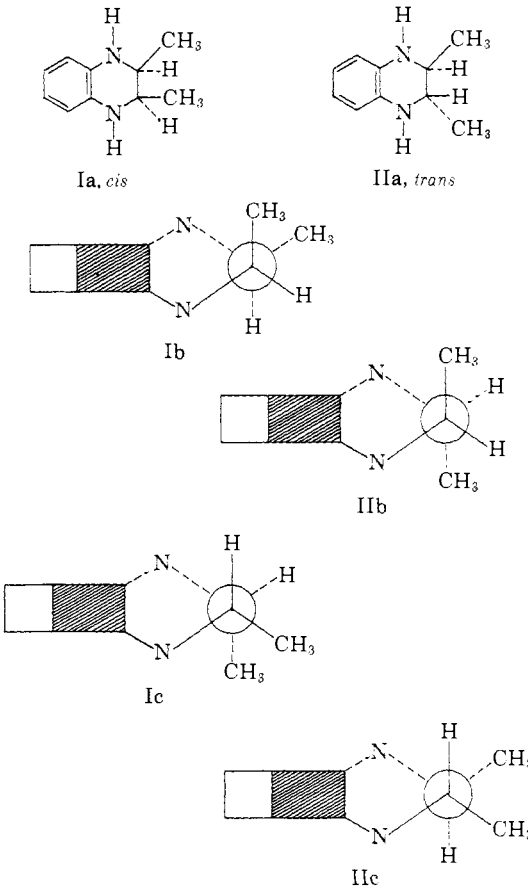
(5) F. Bohlmann, *Ber.*, **85**, 390 (1952).

same melting point obtained earlier by Bergstrom and Ogg[6] from the reaction of methylmagnesium iodide with quinoxaline. This latter product had been assigned the *dl-trans* configuration on the basis of the earlier work of Gibson[7] who had prepared and separated the *trans* and *cis* isomers of 2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (IIa and Ia, m. p. 102–103 and 111–112°, respectively) and established their configuration by resolution of the 102–103° material into its enantiomorphs. Bohlmann pointed out the apparent similarity in the reactions of the Grignard and the lithium aluminum hydride reagents in support of the nature of his product.

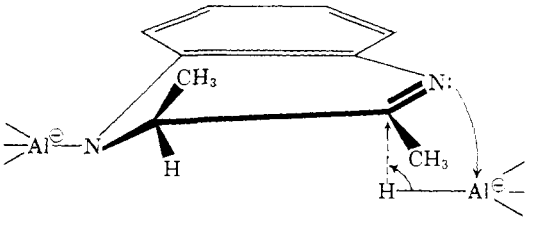
We have repeated the lithium aluminum hydride reduction of 2,3-dimethylquinoxaline, but have isolated only the *cis* isomer Ia, m. p. 113–114°. This was found to be identical with a sample of *cis*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline prepared by the low temperature platinum catalyzed reduction of 2,3-dimethylquinoxaline, and to be non-identical with a sample of the *trans* compound, made by the method of Gibson,[7] as evidenced by mixture melting point and infrared spectra.

The *trans*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline is obviously the energetically preferred isomer as can be seen by reference to the conformational projections represented in Ib, Ic, IIb and IIc in which only one conformation, IIb, is free of skew interactions. Because of eclipsing by the 2,3-substituents the boat forms need not be considered. The hydrogens on the nitrogen atoms may be considered to be equatorially disposed, projecting in front of and behind the plane of the page. Since the lithium aluminum hydride reduction does give the thermodynamically least stable *cis* form I, this must mean that either the hydrogen is transferred in a stereospecific manner or that the product under the conditions of the reaction is isomerized to the *cis* form. Since lithium aluminum hydride does not isomerize the authentic *trans* product to the *cis* form under the reaction conditions, we can safely assume that the hydrogen is transferred stereospecifically. Thus the reduction cannot be by way of a *free* hydride ion unless in some way the two nitrogens of a quinoxaline ring (or the four nitrogen atoms of two quinoxaline rings) are so complexed with a single tetrahedral aluminum atom that only one face of each ring is vulnerable to attack by hydride ion. The normal C–Al bond distance would require that the aromatic nitrogen-containing quinoxaline ring be in a non-planar, boat form which is unlikely. The idea of a π-type complex between the metal hydride and the aromatic ring can hardly explain the results since upon completion of the first stage of reduction, the aromatic nature of the system would be destroyed and with it the π-complex. Thus the free hydride ion mechanism[8] is inadequate as indeed it must be in light of the asymmetric reductions reported by Bothner-By.[9]

It seems more likely that once the first C=N is reduced, the reagent attacks the second nitrogen in



the ring and the hydrogen atom of the reagent is transferred to the carbon atom of the ring from the least hindered side, as represented in III, in a stereospecific manner leading to the *cis* product.



III

This is analogous to the attack of the reactive species from the lithium aluminum hydride on the least hindered side of the carbonyl group in *d*-camphor.[10] In view of these considerations it was of interest to attempt a reduction of the quinoxaline system by using a metal hydride which had only one active hydrogen available. Lithium tri-*t*-butoxyaluminum hydride[11] did not reduce 2,3-dimethylquinoxaline upon heating for 4 hours in tetrahydrofuran.

The lithium aluminum hydride reduction of the corresponding 2,3-dimethyl-1,4,5-(and 1,4,6)-triazanaphthalene gave in each case one product whose stereochemistry was assumed by analogy with the 2,3-dimethylquinoxaline case to be *cis*. Direct chemical proof of *cis* configuration of the triaza-

(6) F. W. Bergstrom and R. A. Ogg, THIS JOURNAL, **53**, 245 (1931).
(7) C. S. Gibson, *J. Chem. Soc.*, 342 (1927).
(8) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publ., Inc., New York, N. Y., 1950, pp. 89, 804.
(9) A. A. Bothner-By, THIS JOURNAL, **76**, 846 (1951).
(10) (a) D. S. Noyce and D. B. Denney, *ibid.*, **72**, 5743 (1950); (b) L. W. Trevor and W. G. Brown, *ibid.*, **71**, 1675 (1949).
(11) H. C. Brown and R. F. McFarlin, *ibid.*, **78**, 252 (1956).

TABLE I

PROPERTIES OF TETRAHYDROPOLYAZANAPHTHALENES AND PRECURSORS

Compound	Melting point, °C.	Ultraviolet spectra: in base λ_{max}, mμ	in base log ϵ_{max}	in alcohol λ_{max}, mμ	in alcohol log ϵ_{max}	in acid λ_{max}, mμ	in acid log ϵ_{max}	Color with $FeCl_3$ [i]
o-Phenylenediamine	104.5–106.0	230[e]	3.88	237[b]	3.85	230[f]	4	Red
		288	3.67	294	3.57	281	3.27	
1,2,3,4-Tetrahydroquinoxaline	98.5–100.5[j]	246[c]	3.78	219[b]	4.45	241[d]	3.81	Purple
		304	3.62	254	3.63	290	3.11	
				310	3.54			
trans-2,3-Dimethyl-1,2,3,4-tetrahydroquinoxaline	104–105[k]	245[c]	3.75	260[b]	3.64	240[f]	4.0	Blue
		300	3.54	310	3.78	295	3.33	
cis-2,3-Dimethyl-1,2,3,4-tetrahydroquinoxaline	114–115	247[c]	3.70	256[b]	3.70	238[d]	4.11	Purple
		303	3.52	312	3.60	283	4.07	
2,3-Diaminopyridine	112–114	237[e]	3.80	233[h]	3.69	215[g]	3.85	Orange
		300	3.78	302	3.80	248	3.66	
						315	3.91	
cis-2,3-Dimethyl-1,2,3,4-tetrahydro-1,4,5-triazanaphthalene	111.5–112.5	254[e]	3.69	260[a]	3.76	235[g]	3.60	Red (slight)
		322	3.85	330	3.91	266	3.57	
						288	3.97	
3,4-Diaminopyridine	208–209[l]	245[e]	3.89	251[b]	3.75	224[f]	4.33	None
		283	3.57	291	3.67	287	3.97	
cis-2,3-Dimethyl-1,2,3,4-tetrahydro-1,4,6-triazanaphthalene	149–150	264[e]	3.65	274[b]	3.60	214[f]	4.29	None
		298	3.65	308	3.73	237	4.22	
						307	3.99	

[a] Ethanol solvent. [b] Methanol solvent. [c] 1 *N* NaOH. [d] 1 *N* HCl. [e] 0.01 *N* NaOH. [f] 0.01 *N* HCl. [g] 0.01 *N* H_2SO_4 [h] Water solvent. [i] Upon adding solid to $FeCl_3$ solution. [j] J. C. Cavagnol and F. Y. Wiselogle, THIS JOURNAL, 69, 795 (1947), report m.p. 98.5–99.0°. [k] References 6 and 7 report m.p. 101–102°. [l] Reference 13 reports m.p. of 218–219°.

naphthalene derivatives was lacking. It was hoped that the infrared spectra might offer a clue as to the stereochemistry of these compounds. When the spectra of potassium bromide pressings of the *cis*- and *trans*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxalines were examined, it was observed that the *cis* isomer I had a strong doublet in the N–H stretching region at 2.96 and 3.02 μ while the *trans* isomer II had only a singlet at 3.02 μ. Furthermore, both of the tetrahydrotriazanaphthalenes had a doublet in this region. In carbon disulfide solvent, however, the *cis* isomer I showed only a single band at 2.98 μ and thus the doublet in the potassium bromide pressing of I must be of crystal origin. The doublets in the triaza analogs must be ascribed to the fused nitrogen containing ring and not to the *cis* configuration.

It can be seen from examining Table I that there are no clear-cut correlations in the ultraviolet spectra which might make it possible to distinguish *cis* and *trans* isomers in this series. In general the ultraviolet spectra of the reduced polyazanaphthalenes resemble those of their diamine precursors. It was noted that *o*-phenylenediamine and the tetrahydroquinoxalines gave colors with ferric chloride whereas the fused pyridine analogs did not. The reason for this may be a strong complexing of the ferric chloride with the pyridine ring which does not take place with the tetrahydroquinoxalines.

Experimental[12]

2,3-Dimethyl-1,4,6-triazanaphthalene. A.—To 1.91 g. (0.0175 mole) of 3,4-diaminopyridine[13] in 20 ml. of dilute hydrochloric acid was added 1.50 g. (0.0175 mole) of biacetyl in 7 ml. of water. The mixture was heated on the steam-bath for 2 minutes and then neutralized with 10% sodium hydroxide solution. The solvent was removed at reduced pressure and from the residue was obtained by sublimation 400 mg. (14% yield) of crude product, m.p. 105–106°. Recrystallization from *n*-hexane and subsequent resublimation at 70° (0.5 mm.) brought the melting point to 123–125° (Kofler).

Anal. Calcd. for $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.00; H, 5.62; N, 26.43.

B. To 5.0 g. (0.046 mole) of 3,4-diaminopyridine suspended in 50 ml. of benzene was added 3.90 g. (0.045 mole) of diacetyl. After 3 hours refluxing under a Dean–Stark apparatus, 1.0 ml. (100% of theory) of water was collected. The benzene solution was treated with Norit, filtered and diluted with twice the volume of petroleum ether. Upon cooling, 4.69 g. (65%) of crude product crystallized. Sublimation (80–90°, 1 mm.) yielded colorless crystals, m.p. 127°.

***cis*-2,3-Dimethyl-1,2,3,4-tetrahydroquinoxaline (I). A. By Lithium Aluminum Hydride Reduction.**—To a stirred solution of 2,3-dimethylquinoxaline (3.2 g., 0.02 mole) in 200 ml. of absolute ether, was added a solution of lithium aluminum hydride (1.2 g., 0.05 mole) in 50 ml. of absolute ether. The mixture was stirred for 6 hours under an inert atmosphere and then decomposed by the cautious addition of 20 ml. of 10% potassium hydroxide. The precipitated aluminum hydroxide was removed by filtration of the reaction mixture. The ether layer and combined ether extract of the aqueous layer were dried over anhydrous sodium sulfate. The residue upon vacuum evaporation was recrystallized from benzene–petroleum ether; 2.25 g. (70%), m.p. 110–113°, and purified by sublimation at 100° (0.3 mm.), m.p. 114–115° (lit.[7] m.p. 111–112°).

B. By Catalytic Reduction.—2,3-Dimethylquinoxaline (25.0 g., 0.158 mole) dissolved in thiophene-free benzene, 185 ml., was shaken for a short time with Raney nickel to remove possible catalyst poisons and then hydrogenated at 6.0 atm. in the presence of 0.23 g. of Adams catalyst until the theoretical amount of hydrogen was taken up (about 20 hr.). After the catalyst had been removed, the solution was warmed for a short time with Norit, filtered and diluted with petroleum ether. The crystals that separated were collected and then washed with petroleum ether; 8.0 g. (30%), m.p. 114.5–115.5°. The mother liquor yielded 7.0 g. (26%) more of this product. This product was identical with the *cis*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline obtained by lithium aluminum hydride reduction as evi-

(12) Melting points are corrected and were taken on a Fisher-Johns block unless otherwise noted. Analyses were by Microchemical Specialties, Berkeley, Calif., or the Research Laboratories, Eastman Kodak Co., Rochester, N. Y.

(13) E. Koenigs, H. Bueren and G. Jung, *Ber.*, **69**, 2690 (1936).

denced by mixture melting point and infrared determinations.

The tetrahydroquinoxaline reported in Table I was prepared by this method, m.p. 98.5–100.5°. Its infrared spectrum showed a single band at 3.08 μ.

dl-trans-**2,3-Dimethyl-1,2,3,4-tetrahydroquinoxaline.**—This authentic sample was prepared by the method of Gibson,[7] m.p. 104–105°. A mixture melting point with the lithium aluminum hydride reduction product was 78–85°. The infrared spectra of this authentic *trans* compound showed a single peak in the NH region at 3.02 μ both in potassium bromide pressing and in carbon disulfide solution, while the *cis* product showed a well defined doublet at 2.96 and 3.02 μ in potassium bromide pressing but a singlet at 2.98 μ in carbon disulfide solution.

The authentic *trans* compound was dissolved in ether and treated with lithium aluminum hydride in the same manner as during the reduction of the quinoxaline. The recovered product melted at 104–105°, did not depress the melting point of the starting material, but lowered the melting point of the *cis* compound to 93–98°.

dl-cis-**2,3-Dimethyl-1,2,3,4-tetrahydro-1,4,5-triazanaphthalene.**—By the same lithium aluminum hydride method as used for 2,3-dimethylquinoxaline there was obtained a 70% yield of this tetrahydro derivative from 2,3-dimethyl-1,4,5-triazanaphthalene,[1,14] m.p. 111.5–112.5° (Kofler).

Anal. Calcd. for $C_9H_{13}N_3$: C, 66.22; H, 8.03; N, 25.75. Found: C, 66.35; H, 7.96; N, 25.69.

dl-cis-**2,3-Dimethyl-1,2,3,4-tetrahydro-1,4,6-triazanaphthalene.**—By the same procedure 2,3-dimethyl-1,4,6-triazanaphthalene[1] (3.20 g., 0.02 mole) was reduced to the tetrahydro compound, 1.80 g. (55%), which was purified by crystallization from benzene–petroleum ether and sublimation, m.p. 149–150°.

Anal. Calcd. for $C_9H_{13}N_3$: C, 66.22; H, 8.03; N, 25.75. Found: C, 66.6; H, 7.8; N, 25.6.

Acknowledgment.—We are indebted to the Eastman Kodak Co., Research Laboratories, Rochester, N. Y., for most of the spectral determinations, to Miss Thelma Davis for help with the spectral correlations and to Mr. John Stenberg for the catalytic hydrogenations.

(14) V. Petrow and J. Saper, *J. Chem. Soc.*, 1389 (1948).

STANFORD, CALIF.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Pteridines. XXII. 5,8-Dihydropteridines by Sodium Borohydride Reduction[1,2]

BY WOLFGANG PFLEIDERER AND EDWARD C. TAYLOR

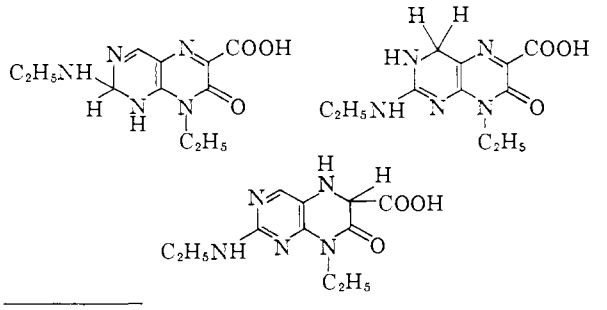
RECEIVED OCTOBER 6, 1959

Sodium borohydride reduction of a number of 8-substituted-7(8*H*)-pteridinone-6-carboxylic acids has been shown to lead to derivatives of 7-hydroxy-5,8-dihydropteridine-6-carboxylic acid. These compounds possess remarkable chemical stability due to intramolecular hydrogen bonding between the 7-hydroxy group and the carbonyl oxygen of the 6-carboxyl group, and their high ultraviolet absorption maxima (405 mμ) are ascribed to the presence in these compounds of a new pteridine chromophoric system. It is suggested that some naturally-occurring reduced pteridines may also be 5,8-dihydro derivatives.

A recent paper from this Laboratory described a new synthetic route to pteridine-6-carboxylic acids which involved the condensation of a 4,5-diaminopyrimidine with alloxan in basic solution, and which proceeded *via* the intermediate formation of a 6-*spiro*pteridine.[3] Certain of the pteridine-6-carboxylic acids prepared during an extension of that study underwent a novel reduction with sodium borohydride, and the present paper describes our investigations on the structure and properties of these dihydropteridines.

The condensation of 2,4-bis-(ethylamino)-5-aminopyrimidine (I) with alloxan in basic solution, or with the disodium salt of mesoxalic acid, proceeded smoothly to give 2-ethylamino-8-ethyl-7-(8*H*)-pteridinone-6-carboxylic acid (II). The structure of II was confirmed by decarboxylation, either by vacuum sublimation or by heating at 200°, to 2-ethylamino-8-ethyl-7(8*H*)-pteridinone (III), which was synthesized independently by condensation of I with ethyl glyoxalate ethyl hemi-acetal. Treatment of II with sodium borohydride in dilute alkaline solution then yielded a dihydro derivative (IV) with rather remarkable physical properties. It exhibited an intense blue fluorescence in solution, possessed a bright yellow color, and comparison of its pK_a with that of the starting material showed that it was 10,000 times a weaker acid. Furthermore, its ultraviolet absorption spectrum exhibited an absorption maximum 48 mμ *higher* than the starting material, and at a wave length (404 mμ) almost unprecedented among simple pteridines.

This latter observation is surprising indeed, for one would intuitively expect disruption of the aromatic system by reduction to result in a hypsochromic shift in the ultraviolet absorption spectrum. Since sodium borohydride does not reduce a carboxyl or amide carbonyl group, there would appear to be only three possible structures for the dihydro acid; namely, the 1,2-, 3,4- or 5,6-dihydro derivatives. Reduction of the 9,10- ring fusion double bond is excluded because of the presence of a second N–H band in the infrared spectrum of the reduced acid. Since it is well known that pyrazine rings are always reduced in preference to pyrimidine rings,[4,5]



(1) For the preceding paper in this series, see E. C. Taylor and C. C. Cheng, *J. Org. Chem.*, **25**, in press (1960).

(2) This work was supported in part by a grant to Princeton University from the American Cancer Society.

(3) E. C. Taylor and H. M. Loux, THIS JOURNAL, **81**, 2474 (1959).

(4) E. C. Taylor and W. R. Sherman, *ibid.*, **81**, 2464 (1959).

(5) A. Albert, *Quart. Revs.*, **6**, 197 (1952).