The pentane solution was washed with water, dried, filtered, and concentrated. Sublimation gave 1.6 g (78%) of **13**, mp 133–137° (lit. mp 135–137°[18] and 150°[9]).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.02; H, 10.22.

endo-**Bicyclo[3.3.1]nonan-2-ol** (**14**). **A.**—To a solution of bicyclo[3.3.1]nonan-2-one (0.5 g, 4 mmoles) in 15 ml of anhydrous methanol was added 1.0 g of sodium borohydride over a period of 30 min. This mixture was stirred for 1 hr; 6 ml of water was added and stirring was continued for an additional 1 hr. The solution was poured into 70 ml of pentane. The pentane solution was washed with water, dried, and filtered. After the pentane was removed by distillation at atmospheric pressure, the alcohol was sublimed. The yield of product, mp 177–178°, was 0.45 g (90%).

B. *endo*-Bicyclo[3.3.1]non-3-en-2-ol (0.1 g, 0.7 mmoles) was dissolved in 5 ml of glacial acetic acid. Reduction was carried out in the presence of 10% palladium on carbon on a microhydrogenation apparatus. The mixture was filtered and the filtrate was poured into 50 ml of pentane. The pentane solution was washed with water, dried, and filtered. The solvent was removed by distillation and the residue was sublimed. The yield of alcohol, mp 175–176°, was 0.08 g (80%).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.98; H, 11.87.

The *p*-nitrobenzoate was prepared and crystallized from an alchol–water mixture to a constant melting point of 100–101°.

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.49; H, 6.81; N, 4.72.

Registry No.—**2**, 10036-06-3; **3**, 10036-07-4; **7**, 10036-08-5; **8**, 10036-09-6; **10**, 10036-10-9; *p*-nitrobenzoate of **10**, 10036-11-0; **11**, 10036-12-1; semicarbazone of **11**, 10036-13-2; **12**, 10060-21-6; *p*-nitrobenzoate of **12**, 10036-14-3; **6**, 10036-15-4; *p*-nitrobenzoate of **6**, 10036-16-5; **21**, 10036-17-6; **19**, 10036-18-7; ethyl *m*-nitrocinnamate, 5396-71-4; **24**, 10039-64-2; **25**, 10036-20-1; **26**, 10036-21-2; **13**, 2568-17-4; **20**, 10036-23-4; **15**, 10036-24-5; **14**, 10036-25-6; *p*-nitrobenozate of **14**, 10036-26-7; **12**, 10036-27-8.

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Stereochemistry and Conformations of Reduced Quinoxalines, Phenazines, and Pteridines[1]

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The proton magnetic resonance spectra of *cis*- and *trans*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline exhibit a chemical-shift difference in the signal for the protons adjacent to the nitrogen at C-2 and C-3. This difference of about 0.5 ppm reflects the unequal shielding of axial and equatorial protons resulting from the diamagnetic anisotropy of the carbon–nitrogen single bond. It is concluded that in both isomers interconversion of conformers is rapid down to −87° and that in the *trans* compounds this signal represents hydrogens which are predominantly axially oriented while in the *cis* compounds this is an average signal representing rapidly interconverting equivalent axial and equatorial hydrogens. Thus in the quinoxaline system in chloroform solvent, there is a chemical shift of about 1 ppm downfield in going from an axial to an equatorial proton. The demonstrated generality of this chemical shift permits the assignment of configurations to reduced triazanaphthalenes, phenazines, and pteridines.

Bouveault–Blanc reduction of 2,3-dimethylquinoxaline gives a mixture of *cis*- and *trans*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (I and II, respectively), which can be separated by fractional crystallization *via* the oxalate salts. The stereochemical assignments are due to Gibson,[3] who resolved the lower melting *trans* isomer (II) into its optically active enantiomorphs, thereby distinguishing it from the nonresolvable *cis* isomer (I). Lithium aluminum hydride reduction of 2,3-dimethylquinoxaline[4] is stereospecific, giving the *cis* isomer (I). Similarly prepared were 2,3-dimethyl-1,2,3,4-tetrahydro-1,4,5-triazanaphthalene (III) and 2,3-dimethyl-1,2,3,4-tetrahydro-1,4,6-triazanaphthalene (IV) which were presumed to have the *cis* configuration. Since Gibson's method for proof of configuration by resolution of the *trans-dl* isomer cannot be utilized in the case of these reduced triazanaphthalenes (III and IV) or similar unsymmetrical molecules, the utility of nmr for this purpose has been investigated.

The proton magnetic resonance (pmr) spectra of I and II (Figure 1) are differentiated by a chemical shift in the signal assigned to the protons adjacent to the nitrogen atoms. The resonance signal for the C-2 and C-3 protons of the *trans* isomer (II) occurs 0.5 ppm upfield from the corresponding signal for the *cis* isomer (I) in deuteriochloroform (and about 0.4 ppm as the hydrochloride in deuterium oxide). Evidence for the generality of this chemical-shift difference is gained from examination of spectra of other isomeric pairs of known stereochemistry. Table I reports the chemical shift for the C-2 and C-3 protons of the *cis* and *trans* isomeric pairs (V and VI) from the reduction of 2,3-diphenylquinoxalines[5] and the corresponding phenazine[6] isomers (VII and VIII). In each case the protons (H_x) from the *trans* isomer are more shielded than those from the corresponding *cis* isomer, and this shielding difference is manifest in the observed chemical shift difference of about 0.5 ppm.

A comparison of the chemical shifts of the signals from the C-2 and C-3 protons of reduced triazanaphthalenes III (3.52 ppm) and IV (3.50 ppm) and reduced pteridine IX (3.43 ppm) to the corresponding signals from I (*cis*, 3.48 ppm) and II (*trans*, 2.98 ppm) of established configuration, strongly supports the *cis* con-

(1) Taken in part from the Ph.D. Dissertation of R. A. Archer, Stanford University, 1963.

(2) Parke, Davis Fellow, 1960–1963.

(3) C. S. Gibson, *J. Chem. Soc.*, 342 (1927).

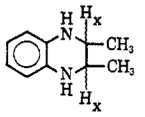
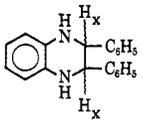
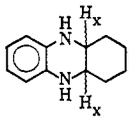
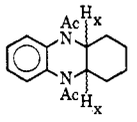
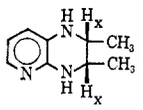
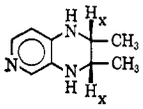
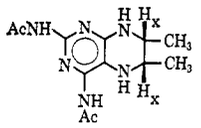
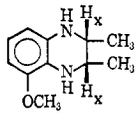
(4) R. C. DeSelms and H. S. Mosher, *J. Am. Chem. Soc.*, **82**, 3762 (1960).

(5) C. S. Gibson, *J. Chem. Soc.*, 1570 (1923).

(6) G. R. Clemo and H. McIlwain, *ibid.*, 258 (1936).

TABLE I

PMR CHEMICAL SHIFTS OF H_x IN TETRAHYDROQUINOXALINES AND RELATED COMPOUNDS

Structure	No., configuration	H_x, ppm[a]	*cis*-H_x − *trans*-H_x, ppm
	I, *cis*[b]	3.48	0.50
	II, *trans*[c]	2.98	
	V, *cis*	4.68	0.52
	VI, *trans*	4.16	
	VII, *cis*[d]	3.30	0.43
	VIII, *trans*[e]	2.87	
	XII, *cis*	4.90	0.65
	XIII, *trans*	4.25	
	III, *cis*	3.52	
	IV, *cis*	3.50	
	IX, *cis*	3.43	
	XIV, *cis*	3.35	

[a] Spectra were taken on a Varian A-60 nmr spectrophotometer in deuteriochloroform. Chemical shifts are reported in parts per million (ppm) relative to internal tetramethylsilane (TMS). [b] The methyl doublet in $CDCl_3$ solvent was centered at 1.11 ppm (J = 7 cps). In D_2O solvent as the hydrochloride the methyl doublet was centered at 1.70 ppm (J = 7 cps) and H_x multiplet was centered at 4.28 ppm. [c] The methyl doublet in $CDCl_3$ solvent was centered at 1.12 ppm (J = 6 cps). In D_2O–DCl solvent the methyl doublet was centered at 1.85 ppm (J = 6 cps) and H_x multiplet was centered at 3.85 ppm. [d] The methylene multiplet was centered at approximately 1.60 ppm, half-height width = 17 cps. [e] The methylene multiplet was centered at approximately 1.54 ppm, half-height width = 45 cps.

figurational assignment for III, IV, and IX. This is the same assignment which would be made on the basis of the previously observed stereospecific *cis* lithium aluminum hydride reduction.[4] The fact that III, IV, and IX have about the same chemical shift for the corresponding C-2–C-3 proton signals indicates that substitution in the aromatic ring has little effect on these chemical shifts. Furthermore, the pmr spectrum of the 5-methoxy-2,3-dimethyltetrahydroquinoxaline prepared by the lithium aluminum hydride reduction of 5-methoxyquinoxaline, presumably therefore

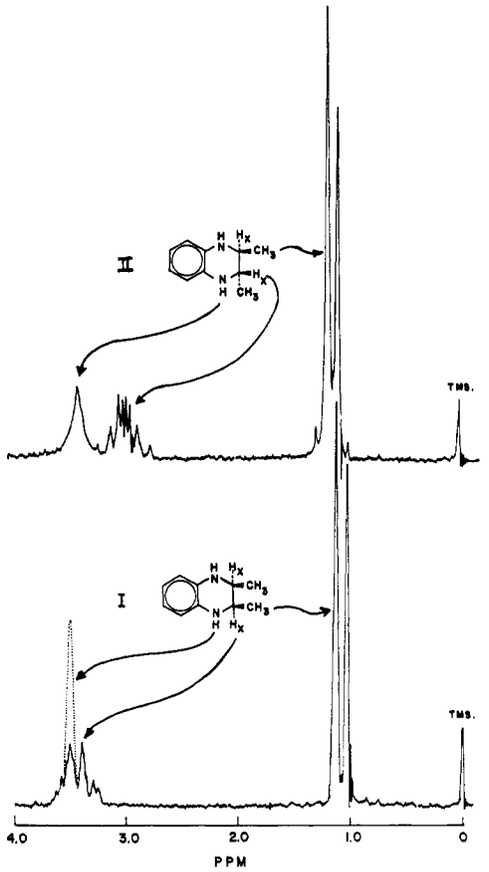
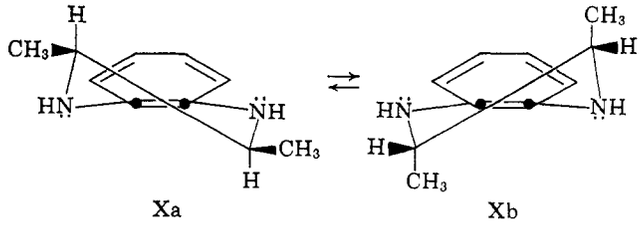


Figure 1.—Nmr spectra of *trans*- and *cis*-1,2,3,4-tetrahydroquinoxaline; chemical shift in parts per million relative to tetramethylsilane (TMS). The dotted line shows the N–H signal which was "washed out" with D_2O.

cis, shows the corresponding signals centered at 3.35 ppm. Thus, the effect of a substituent in the aromatic ring on the signal of C-2, C-3 protons is not large.

The *trans*-octahydrophenazine (VIII) exists of necessity in a rigid conformation with axial hydrogens at the C-4a–C-10a ring juncture. Consequently, the observed resonance for the H_x hydrogens at 2.85 ppm must be assigned to the pure axial orientation. Because of the similarity of chemical shift values of H_x for VIII and II (Table I), it is concluded that the *trans*-tetrahydroquinoxaline (II) must exist predominantly in the half-chair form (Xa) with both C-2 and C-3 methyl groups equatorially oriented rather than in form Xb with the methyl groups axially oriented. Because of the results from temperature studies, *vide infra*, we concluded that there is a rapid interconversion of conformers with the equilibrium ratio greatly favoring Xa.



Xa Xb

It is not obvious *a priori* that the half-chair form with equatorial substituents would be the favored conformation in the 2,3-disubstituted tetrahydroquinoxaline system. Whereas in the cyclohexane chair conforma-

tion there are two 1,3-diaxial interactions for each substituent, in the 2,3-disubstituted tetrahydroquinoxaline system, two of the 1,3-diaxial interactions have been eliminated by virtue of the fused aromatic ring. Furthermore, the two remaining 1,3-diaxial interactions will be with the nonbonding electron pairs on nitrogen which are conjugated with the benzene ring. The conformational preference for a nonbonding electron pair on nitrogen in saturated six-membered rings has been investigated in several systems.[7] In piperidine this lone pair prefers the equatorial position over hydrogen[7a] while in piperazine[7b,d] hydrogen appears to prefer the equitorial conformation over the electron pair by about 0.4 kcal/mole. From the evidence of Brignell, Katritzky, and Russell obtained on substituted 4-piperidones it appears that a 1,3-methyl–nonbonded electron pair interaction would be less than a 1,3-methyl–hydrogen interaction but the difference is not likely to be large. However no evidence from a system strictly comparable with the quinoxalines under study here appears to be available since in the quinoxaline system the nonbonded electron pair on nitrogen is conjugated with the aromatic ring. The extent to which the NH of the quinoxaline system is coplanar with the aromatic ring is in doubt based upon the recent microwave determination which shows that the NH_2 group of aniline is noncoplanar with the benzene ring.[8]

cis-Octahydrophenazine (VII) exists as a rapidly equilibrating mixture of two equivalent half-chair forms, since it shows a single, unresolved multiplet signal for the C-4a and C-10a protons. Any fixed conformation would necessarily show nonequivalent signals for these two protons. Furthermore, the rather narrow methylene range in the pmr spectrum of VII compared to VIII can be ascribed to such conformational mobility.[9]

It is assumed that the observed H_x multiplet centered at 3.30 ppm in the pmr spectrum of VII which is 0.43 ppm downfield from the corresponding signal of the *trans* isomer, is an average chemical shift for the axial and equatorial protons, and it follows, therefore, that the *cis* quinoxaline (I) exists at room temperature as a rapidly equilibrating mixture of equivalent half-chair forms with one axial and one equatorial proton.

From this it follows that the position of the signal for an equatorial hydrogen next to nitrogen in the quinoxalines in chloroform solvent is about 1 ppm downfield from the equivalent axial proton. The possibility that I exists in a half-boat form which would also have a single resonance for the C-2 and C-3 protons can be eliminated on the basis of the corresponding chemical shifts of I (3.48 ppm) and VII (3.30 ppm).

Temperature studies are compatible with this interpretation. When either *cis*- or *trans*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (I or II) was heated in bromobenzene to 140° there was no significant change in the pmr spectrum.[10] Carbon disulfide was unsuitable as a solvent for the low-temperature study because of chemical reaction with the quinoxalines. With perdeuterioacetone solvent there was no significant change in the spectrum of either I or II down to −87°. In dimethyl ether solvent there was no change in the methyl proton signal of I to −138°, but unfortunately, the C-2–C-3 protons of I were obscured by the strong solvent resonance signal. It thus appears that the inversion of the ring in both I and II ($Xa \rightleftarrows Xb$) is still fast on an nmr time scale at a temperature down to −87° and probably below in contrast to cyclohexane, whose inversion becomes measureable by pmr techniques at −65°.

Long-range deshielding effects associated with the benzene ring currents were considered as a possible factor in the observed chemical shift differences. Calculations based upon the work of Johnson and Bovey[11] using distances obtained from measurements on Dreiding models, show that both the axial and equatorial C-2 and C-3 hydrogens are in the deshielding region with the axial hydrogens shielded relative to the equatorial hydrogens by a factor of approximately 0.1 ppm. Thus, although the effect associated with the benzene ring currents is in the proper direction, the magnitude is in the order of one-tenth of the chemical shift difference of approximately 1 ppm actually observed for axial–equatorial protons next to nitrogen in the quinoxaline system when measured in chloroform.

Since the relative shift between axial and equatorial hydrogens is a function of the diamagnetic anisotropy of nearby bonds or rings and the inductive effects of neighboring groups or atoms,[12] the chemical shift difference must have its origin in effects associated with the diamagnetic anisotropy of the carbon–nitrogen single bond. That this anisotropy could give rise to a chemical shift of about 1 ppm between the signals for axial and equatorial protons next to nitrogen in quinoxalines appears reasonable in view of the following. Yamaguchi, *et al.*,[13] have calculated that the anisotropy of cyclic tertiary amino nitrogen is close to the value calculated for the carbon–carbon single bond.[14] Effects of between 0.5 and 1.0 ppm for the chemical shift difference between axial and equatorial protons next to heteroatoms have been reported for cyclohexylamines,[15] sugar acetates,[16] and acylaminocyclitols.[17] Studies on quinolizidine,[18] piperidines,[7a] piperazines,[7b,d,e] and mor-

(7) (a) J. B. Lambert and R. G. Keshe, *J. Am. Chem. Soc.*, **88**, 620 (1966); (b) N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *ibid.*, **87**, 1232 (1965); (c) P. J. Brignell, A. R. Katritzky, and P. L. Russell, *Chem. Commun.*, 723 (1966); (d) R. K. Harris and R. A. Spragg, *ibid.*, 314 (1966); (e) J. Abraham and D. B. MacDonald, *ibid.*, 188 (1966); (f) R. F. Farmer and J. Hamer, *ibid.*, 866 (1966). See M. Hanack, "Conformational Theory," Academic Press Inc., New York, N. Y., 1965, pp 302–314, for a review of prior literature.

(8) D. G. Lester and J. K. Tyler, *Chem. Commun.*, 152 (1966).

(9) (a) G. Booth, *Tetrahedron*, **19**, 91 (1963); (b) J. Musher, *J. Am. Chem.* 1146 (1961).

(10) Perdeuteriodimethyl sulfoxide was unsuitable as a solvent for these high-temperature studies. When I was heated in this solvent, the pmr signal for the C-2–C-3 protons coalesced at 103° to a broad peak which became a sharp multiplet (somewhat obscured by the small DOH peak which migrated from 3.60 ppm at room temperature to 2.90 ppm at 140°) at 117° or above but this process was not reversed upon cooling. Even though the original compound (I) could be recovered unchanged from the solution, some reaction with the solvent must have taken place. Approximately the same observation was made on II.

(11) C. E. Johnson and F. H. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(12) E. Campaigne, N. F. Chamberlain, and B. E. Edwards, *J. Org. Chem.*, **27**, 135 (1962).

(13) S. Yamaguchi, S. Okuda, and N. Nakagawa, *Chem. Pharm. Bull.* (Tokyo), **11**, 1465 (1963).

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 115.

(15) E. L. Eliel, E. W. Della, and T. H. Williams, *Tetrahedron Letters*, 831 (1963).

(16) R. U. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

(17) F. W. Lichtenholer, *Ber.*, **96**, 2047 (1962).

(18) (a) F. Bohlman, D. Schumann, and H. Scheulze, *Tetrahedron Letters* 173 (1965); (b) H. Boaz, unpublished results; (c) T. M. Moyneham, K. Schofield, R. A. Y. Jones, and A. R. Kalritzky, *Chem. Commun.*, 218 (1966).

pholines[7d] have shown that the chemical-shift difference between axial and equatorial protons adjacent to the nitrogen atom are of the order of 0.8 ppm.[18]

An alternative view of the cause for the chemical shift differences considers the shielding effect on protons *trans* diaxial to the unshared pair of nitrogen electrons as suggested for the benzo[*a*]quinolizidines.[19] This shielding would occur if the longitudinal magnetic susceptibility of the lone pair is larger than the transverse susceptibility.[19] In this respect, it is important to note that the lone pair on the nitrogen of the quinoxaline nucleus is conjugated with the aromatic rings (as shown by the ultraviolet spectra) and thus the nitrogen atom with its three substituents must be more nearly planar than in the fully saturated piperidine, piperazine, or morphaline systems, although it is not necessarily coplanar.[8] In the diacetylphenazine pair (XII and XIII) this conjugation of the electron pair on nitrogen is extended into the acetyl group and the chemical shift difference between the C-2–C-3 proton signals in these two compounds at room temperature is increased somewhat from 0.43 ppm in the nonacetylated compound to 0.65 in the acetylated derivative. Consequently, chemical-shift differences between axial and equatorial protons next to nitrogen appear to be dependent in some degree upon the extent of delocalization of the lone electron pair on nitrogen.

Experimental Section[20]

cis-**2,3-Dimethyl-1,2,3,4-tetrahydroquinoxaline** (**I**).—The method of DeSelms and Mosher[4] was followed and the product was further purified by vacuum sublimation at 100° (0.3 mm): mp 113–114°; λ_{max}^{MeOH} 218, 256, and 310 mμ (log ε 4.38, 3.70, and 3.60).

trans-**2,3-Dimethyl-1,2,3,4-tetrahyroquinoxaline** (**II**).—The procedure of Gibson[3] was followed: mp 103–104; λ_{max}^{MeOH} 219, 256, and 310 mμ (log ε 4.50, 3.66, and 3.60).

cis-**2,3-Dimethyl-1,2,3,4-tetrahydro-1,4,5-triazanaphthalene** (**III**) **and** *cis*-**2,3-Dimethyl-1,2,3,4-tetrahydro-1,4,6-triazanaphthalene** (**IV**).—These compounds were prepared by R. C. DeSelms.[4]

cis-**2,3-Diphenyl-1,2,3,4-tetrahydroquinoxaline** (**V**).—The procedure of Maffei and Pietra[21] was used: mp 141–142°; λ_{max}^{MeOH} 219, 250 (shoulder), and 315 mμ (log ε 4.60, 3.74, and 3.80).

trans-**2,3-Diphenyl-1,2,3,4-tetrahydroquinoxaline** (**VI**).—This was synthesized and purified according to the directions of Gibson:[5] mp 105°; λ_{max}^{MeOH} 219, 255, and 314 mμ (log ε 4.65, 3.83, and 3.83).

cis- **and** *trans*-**1,2,3,4,4a,5,10,10a-Octahydrophenazine** (**VII and VIII**).—The procedure of Clemo and McIlwain[6] was employed. VII had mp 145–146°; λ_{max}^{MeOH} 220, 258, and 312 mμ (log ε 4.51, 3.74, and 3.66). VIII had mp 154–155°; λ_{max}^{MeOH} 219, 258, and 308 mμ (log ε 4.52, 3.83, and 3.62).

2,4-Diacetamido-6,7-dimethylpteridine (**XI**).—A slurry of 1.0 g (52 mmoles) of 2,4-diamino-6,7-dimethylpteridine[22] in 40 ml of acetic anhydride was heated on a hot plate and stirred until the pteridine dissolved and a fluorescent red solution resulted. The solution was slowly cooled to room temperature and then poured onto ice to give 0.85 g (60% yield) of a light pink, crystalline solid which progressively darkened without melting upon heating. Recrystallization from chloroform–petroleum ether (bp 30–60°) gave a white, crystalline solid, $\lambda_{max}^{CHCl_3}$ 252 and 345 mμ (log ε 4.68 and 4.18).

Anal. Calcd for $C_{12}H_{14}N_6O_2$: C, 52.50; H, 5.15; N, 30.65. Found: C, 52.65; H, 5.29; N, 30.30.

cis-**6,7-Dimethyl-2,4-diacetamido-5,6,7,8-tetrahydropteridine** (**IX**).—A solution of 0.55 g (2 mmoles) of XI in methanol was hydrogenated over platinum oxide catalyst at room temperature for 8 hr. The solution turned from an initially light yellow color to colorless during the course of the reduction. After removal of the catalyst by filtration under nitrogen and evaporation of the solvent under vacuum, light yellow crystals (0.43 g, 77%) were obtained, which were recrystallized from chloroform–petroleum ether (bp 30–60°): $\lambda_{max}^{0.1\ N\ NaOH}$ 219 and 304 mμ (log ε 4.29 and 3.95), λ_{min} 262 mμ (log ε 3.73).

Anal. Calcd for $C_{12}H_{18}N_6O_2$: C, 51.78; H, 6.52; N, 30.20. Found: C, 50.38; H, 6.57; N, 29.84.

cis- **and** *trans*-**1,4-Diacetyl-1,2,3,4,4a,5,10,10a-octahydrophenazine** (**XII and XIII**).—The procedure of Morley[23] was employed for the preparation of these two acetyl derivatives.

cis-**5-Methoxy-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline.**—A solution of 500 mg of 5-methoxy-2,3-dimethylquinoxaline[24] in 95% ethanol was hydrogenated over Adams catalyst for 2 hr. Filtration and evaporation to dryness under nitrogen gave a clear yellow oil whose nmr ($CDCl_3$) showed δ 1.01 (6 H, doublet, J = 6 cps), 3.38 (2 H, quantet, J = 6 cps), 3.50 (2 H, singlet, lost with D_2O), 3.68 (3 H, singlet), and 6.02–6.49 ppm (3 H, multiplet).

Registry No.—I, 7739-04-0; II, 7739-05-1; V, 7739-06-2; VI, 7739-07-3; VII, 7739-08-4; VIII, 7739-09-5; XI, 7739-10-8; IX, 7739-11-9; XIV, 7739-12-0; XII, 4121-38-4; XIII, 7739-14-2; III, 7739-15-3; IV, 7739-16-4.

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