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REDUCTION OF QUINOXALINE-DI-N-OXIDES WITH SODIUM BOROHYDRIDE[1]

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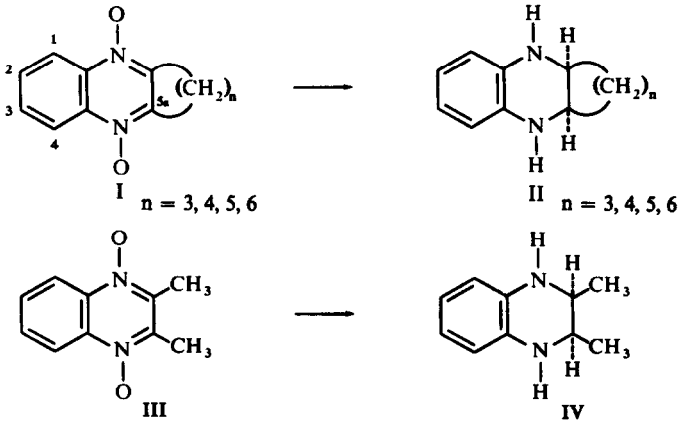
Abstract—The reduction of a number of 2,3-disubstituted quinoxaline-di-N-oxides with sodium borohydride gave predominantly *cis*-2,3-disubstituted 1,2,3,4-tetrahydroquinoxalines in good yield. Treatment of the same quinoxaline-di-N-oxides with sodium dithionite gave the corresponding quinoxalines. Reduction of the latter with metallic sodium afforded *trans*-2,3-disubstituted 1,2,3,4-tetrahydroquinoxalines.

Evidence in support of a postulated reaction mechanism for the reduction of quinoxaline-di-N-oxides with sodium borohydride is presented.

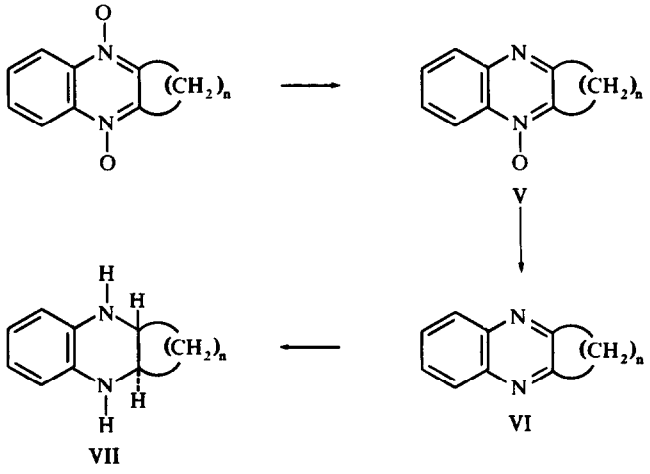
NITRONES are reported[2] to yield N-hydroxylamines upon treatment with complex metal hydrides; however, little is known about the reduction of aromatic amine oxides with complex metal hydrides.[3]

Quinoxaline-di-N-oxides resemble nitrones, to the extent that the former can be considered as bis-nitrones, and hence are expected to give N,N'-dihydroxy-1,2,3,4-tetrahydroquinoxaline upon reduction with complex metal hydrides. Yet the reaction products of 6,7,8,9-tetrahydrocyclohexa[*b*]quinoxaline-di-N-oxide[4, 5] (I, n = 4) with sodium borohydride in methanol were *cis*-5,5a,6,7,9,9a,10-octahydrocyclohexa[*b*]-quinoxaline (II, n = 4) and the *trans*-isomer in a 9:1 ratio. Product II (n = 4) was identical with an authentic sample prepared by the method of Clemo and McIlwain.[6] Treatment of 2,3-dimethylquinoxaline-di-N-oxide (III) with sodium borohydride yielded *cis*-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (IV), which was identical to the product obtained from LAH reduction of 2,3-dimethylquinoxaline.[7] Similarly, the reduction of quinoxaline di-N-oxides I (n = 3,5,6) gave the corresponding *cis*-tetrahydroquinoxalines II (n = 3,5,6).



Products II and IV show N—H absorption bands in the IR at 3300–3320 cm^{-1}, and C—N bands at 1290–1300 cm^{-1}. The NMR spectra of these tetrahydroquinoxalines show peaks for aliphatic protons in the 8·5 τ region, N—H and CH—N-protons at around 6·6 τ, and aromatic protons at 3·5 τ.

In order to confirm the *cis*-ring junction in products II, it was essential that the *trans*-isomers be prepared for comparison. The reduction of the quinoxaline-di-N-oxide I (n = 3,4,5,6) with sodium dithionite yielded the corresponding quinoxaline VI (*n* = 3, 4, 5, 6). The reduction can be stopped at the mono-N-oxide (V) stage, which most probably is an intermediate in this reaction.



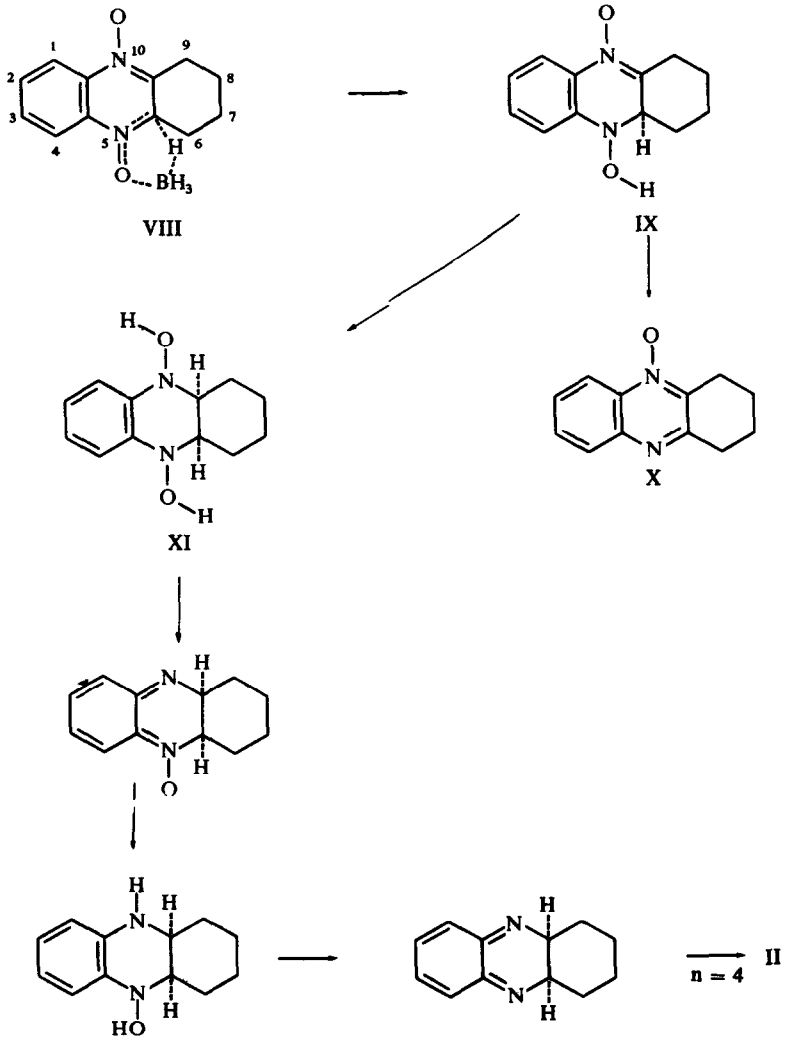
Further reduction of quinoxaline VI (n = 3,4,5,6) with sodium in absolute ethanol gave *trans*-tetrahydroquinoxaline VII (n = 3,4,5,6). It was hoped that the *cis*-tetrahydroquinoxalines II could be differentiated from their *trans*-isomers (VII) by NMR, especially via the difference in the coupling constants of the protons at the ring junction; however, although slight differences were observed in the NMR spectra of the *cis*- and *trans*-series (II and VII), and in the spectra of their respective N,N′-diacetyl derivatives, they were not conclusive enough to establish a general criterion for differentiation. Nonetheless, N,N′-diacetyl derivatives of II showed an UV maximum centered at 227 mu while the N,N′-diacetyl derivatives of the *trans*-isomers (VII) displayed a peak centered at 223 mu.

The mechanism of the reaction of quinoxaline-di-N-oxides I (n = 3,4,5,6) with sodium borohydride is discussed below, using 6,7,8,9-tetrahydrocyclohexa[*b*]quinoxaline-di-N-oxide (I, n = 4) as a model (scheme I). The first step in this mechanism is postulated to involve coordination between the boron atom of the borohydride moiety and the oxygen of the N-oxide, and a synchronous transfer of a hydride ion to C_{5a} (transition state VIII), which eventually leads to intermediate IX. The latter can either lose a molecule of water to give monoxide X (path b), or undergo further hydride reduction to yield XI (path a). The steric bulk of the methylene group at C_{5a} renders the approach of the hydride ion *trans*- to this methylene more feasible, and therefore results in the formation of a predominantly *cis*- ring junction at C_{5a} and C_{9a}.[8,9]

The possibility that monoxide X might be a major intermediate in this reaction

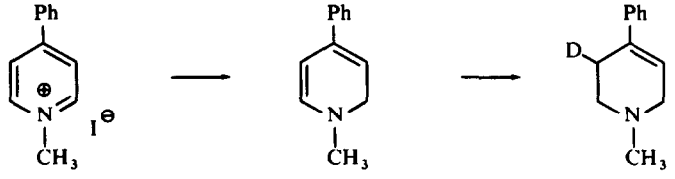
was dismissed because an independently synthesized monoxide X, when subjected to the conditions of the reaction, gave an equimolar mixture of *cis*- and *trans*-tetrahydroquinoxaline II (n = 4), and therefore showed a lack of stereospecificity. On the other hand, the isolation of *trans*- II (n = 4) as a minor product in scheme 1 could be due to the formation and subsequent reduction of monoxide X. It is evident that monoxide X, if formed at all, is a minor intermediate. Another plausible intermediate is quinoxaline VI (n = 4). However, the latter was recovered unchanged under the reaction conditions, and therefore cannot be considered a reaction intermediate. The postulated intermediate XI can be envisaged to undergo two consecutive steps, each of which involves a 1,4-elimination followed by a reduction with sodium borohydride, leading to product II (n = 4).

SCHEME I



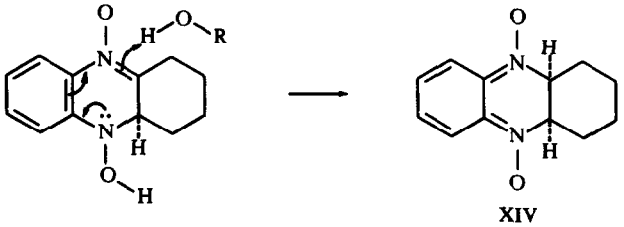
The conversion of XI into II can be postulated to proceed by the displacement of the OH group by a hydride ion, yet this displacement is unlikely in view of the fact that the reduction of nitrones is known to stop at the N-hydroxylamine stage.

Moreover, the properties of aromatic amine oxides can be related to those of heterocyclic iminium ions. The reduction of the latter, especially pyridinium salts, with sodium borohydride has recently received extensive attention.[10] For example, it was shown that 4-phenylmethylpyridinium iodide, when reduced with sodium borohydride-deuterium oxide, gave 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine with a deuterium atom at position 3.[11]



XII XIII

The incorporation of deuterium at position 3 in product XIII showed that intermediate XII reacted with solvent. Such reaction can be conceived to occur between intermediate IX and the solvent to give intermediate XIV, assuming that the interaction with solvent is faster than the reduction with hydride ion (path a). We examined



XIV

this possibility by the reduction of quinoxaline-di-N-oxide I (n = 4) with sodium borodeuteride. The product, d_2-tetrahydroquinoxaline II (n = 4), showed no NMR bands for the protons at the ring junction (C_{5a} and C_{9a}). Mass spectral analysis of the N,N'-diacetyl derivative of this product showed that it contained two deuteriums per molecule and no bands for the protons at C_{5a} and C_{9a} in the NMR spectrum. Furthermore, the reduction of monoxide X with sodium borodeuteride gave a *cis-trans*-mixture of d_2-tetrahydroquinoxaline II (n = 4) with deuterium atoms at positions 5a and 9a. These findings support the mechanism that involves a hydride ion attack at positions 5a and 9a and exclude a mechanism whereby a proton at either position is supplied by the solvent.

In conclusion, sodium borohydride was shown to reduce a number of substituted quinoxaline-di-N-oxides to *cis*-tetrahydroquinoxalines as predominant products, while the reduction of substituted quinoxalines with sodium in absolute ethanol gave the *trans*-isomers. These reactions seem to be general and constitute simple methods for the synthesis of tetrahydroquinoxalines in good yield.

EXPERIMENTAL*

General procedure for the reduction of quinoxaline-di-N-oxides with sodium borohydride

Procedure A. As a typical example, I(n = 4; 1 g) was dissolved in MeOH by warming. An ethanolic suspension of $NaBH_4$ (0·5 g) was added in portions to the stirred soln. The mixture was heated for 2 min, during which it developed a purple colour which faded into pale yellow. The soln was diluted with water and left to stand in a cold bath for 1 hr; the resulting product, *cis*-5,5a,6,7,8,9,9a,10-octahydro[*b*]quinoxaline, was collected (0·48 g), m.p. 140–142°. Recrystallization from MeOH or light petroleum gave colorless plates, m.p. 147°. The product gave a blue color with $FeCl_3$, and showed a single spot on TLC with benzene-MeOH (100:1) as eluent. This spot acquired a blue coloration upon exposure to I_2 vapours.

IR: 3320, 3300, 1600, 1370, 1290, 1060, 910, 735, 715 cm^{-1}; NMR: broad multiplet centered at 8·34 (8 H), broad singlet at 6·53 (4 H), singlet at 3·48 (4 H). In deuterated chloroform-trifluoroacetic acid: multiplets at 8·84 (8 H), and 4·15 (2 H), singlet at 2·9 (4 H). (Found: C, 76·71; H, 8·57; N, 14·76. calc. for $C_{12}H_{16}N_2$: C, 76·55; H, 8·57; N, 14·88).

Extraction of the mother liquor with ether and evaporation of the dried ether gave a residue which, upon TLC and development with I_2 vapour, showed a blue spot due to *cis*-II (n = 4) and a purple coloration for the *trans*-II (n = 4). The identity of the latter was confirmed by comparison with an authentic sample. The ratio of *cis*-5,5a,6,7,8,9,9a,10-octahydro[*b*]quinoxaline to the *trans*-isomer was estimated as 9:1 from the IR spectrum of the crude product (bands at 1290–1310 cm^{-1}).

The above reaction was conducted in THF or acetonitrile as solvents, and gave the same results in both solvents.

The above reaction was repeated using $NaBD_4$. The deuterated *cis*-5,5a,6,7,8,9,9a,10-octahydro[*b*]quinoxaline showed multiplets centered at 8·5 (8 H), and 6·75 (2 H), and a singlet at 3·5 (4 H). In trifluoroacetic acid the deuterated product showed a doublet centered at 8 (8 H), and a singlet at 2·6 (4 H).

cis-2,3-*Dimethyl*-1,2,3,4-*tetrahydroquinoxaline* (IV). 2,3-Dimethylquinoxaline-di-N-oxide (0·5 g) gave, on reduction with $NaBH_4$,-*cis*-IV (0·24 g). On recrystallization from light petroleum, the product melted at 109–111° (lit.[12] 112–113). IR: 3320, 3300, 1600, 1370, 1290, 1010, 920, 740 cm^{-1}.

cis-5,5a,6,7,8,8a,9-*Heptahydrocyclopenta*[b]*quinoxaline* (II, n = 3). 7,8-Dihydro-6H-cyclopenta[*b*]quinoxaline-di-N-oxide was reduced according to procedure A and yielded *cis*-5,5a,6,7,8,8a,9-heptahydrocyclopenta[*b*]quinoxaline which was recrystallized from light petroleum to give plates, m.p. 104°; TLC revealed one spot; IR: 3320, 1600, 1370, 1290, 737 cm^{-1}; NMR multiplet at 8·3 (6 H), broad singlet at 6·46 (4 H), singlet at 3·5 (4 H). (Found: C, 75·84; H, 8·09; N, 16·27. calc. for $C_{11}H_{14}N_2$: C, 75·82; H, 8·10; N, 16·08%).

cis-5,5a,6,7,8,9,10,10a,11-*Nonahydrocyclohepta*[b]*quinoxaline* (II, n = 5). Reduction of 7,8,9,10-tetrahydro-6*H*-cyclohepta[*b*]quinoxaline-di-N-oxide (1·5 g) according to procedure A afforded the title product (1·3 g) which, on recrystallization from light petroleum, melted at 123–124°. One spot on a TLC plate was observed. IR: 3310, 3290, 1600, 1300, 1110, 920, 740 cm^{-1}; NMR: broad multiplet at 8·4 (10 H), broad singlets at 6·62 (4 H), and 3·52 (4 H). (Found: C, 77·05; H, 8·55; N, 14·01. calc. for $C_{13}H_{18}N_2$: C, 77·18; H, 8·97; N, 13·85%).

cis-5,5a,6,7,8,9,10,11,11a,12-*Decahydrocycloocta*[b]*quinoxaline* (II, n = 6). 6,7,8,9,10,11-hexahydrocycloocta[*b*]quinoxaline-di-N-oxide (3 g) was dissolved in EtOH. $NaBH_4$ (1·5 g) was added, and the temp of the mixture was kept below 40° by cooling when necessary. After 30 min an additional amount of $NaBH_4$ (0·5 g) was added. The soln was allowed to stand at room temp for 2 h. Dilution with water gave a yellow solid (2·3 g). The product was chromatographed over neutral alumina using light petroleum and benzene as eluents. The fractions that gave a positive $FeCl_3$ test were combined and recrystallized from light petroleum. The analytical sample of *cis*-5,5a,6,7,8,9,10,11,11a,12-decahydrocycloocta[*b*]quinoxaline melted at 124°; IR: 3310, 3280, 1600, 1290, 740 cm^{-1}; NMR: broad singlets at 8·4 (12 H), 6·52 (4 H), and 3·52 (4 H).

* M.ps are uncorrected. Alumina used for column chromatography was neutral, Grade 1 "Woelm" to which 3% water was added. Freshly prepared silica gel plates were used in thin layer chromatography. Infrared spectra were taken in Nujol using a Perkin–Elmer infrared spectrophotometer Model 257. UV spectra were determined in MeOH soln in a Perkin–Elmer UV-Visible-NIR Spectrophotometer Model 450. Unless mentioned otherwise, NMR spectra were run in deuterated chloroform on a Varian A-60 D spectrometer, and the data are reported in values with TMS as an internal standard. Elemental analyses were performed by F. Pascher, Bonn, Germany.

6,7,8,9-*Tetrahydrocyclohexa*[b]*quinoxaline mono*-N-*oxide* (X). A soln of 6,7,8,9-tetrahydrocyclohexa[*b*]-quinoxaline (3 g) in 40% peracetic acid (10 ml) was warmed gently. When the reaction became exothermic, it was immediately diluted with water and allowed to stand at room temp overnight. The crystalline solid was collected, washed thoroughly with water, and dried, m.p. 120–125°. The product was chromatographed over neutral alumina and eluted with light petroleum-benzene 1:1. The product, monoxide X, m.p. 87–96°, is hygroscopic, as evidenced by the appearance of a broad hydroxy band in the IR spectrum, which disappeared upon removing the water of crystallization with benzene; IR: 3300–3400 (broad), 1580, 1350, 1330 (N—O), 1310, 1170, 1124, 1105, 1090, 979, 940, 875, 765 cm^{-1}; NMR (CCl_4): multiplets centered at 8·08 (4 H), 7 (4 H), 2·36 (3 H), and 1·56 (1 H).

Reduction of 6,7,8,9-*tetrahydrocyclohexa*[b]*quinoxaline mono*-N-*oxide with sodium borohydride*

Procedure A was followed in the reduction of the title compound (0·5 g), and the product melted at 120–123°. TLC of this product, with benzene-MeOH (100:1) as eluent, showed two spots of about the same intensity, identical to those shown by an authentic equimolar mixture of *cis*- and *trans*-5,5a,6,7,8,9,9a,10-octahydrocyclohexa[*b*]quinoxaline. Separation of the two isomers could be effected by careful column chromatography. The IR spectrum of the product was identical to that of a known mixture of the *cis*- and *trans*-isomers. The characteristic band for the *cis*-isomer at 1300 cm^{-1} was of about the same intensity as the band for the *trans*-isomer at 1310 cm^{-1}; IR: 3320 (doublet), 3303, 1600, 1310, 1290, 1060, 940, 920, 910, 740 cm^{-1}; NMR: broad multiplet at 8·5 (8 H), broad singlets at 6·62 (2 H), and 3·5 (4 H).

The above reduction was repeated using $NaBD_4$. A mixture of the *cis*- and *trans*-isomers of II (n = 4) was obtained, the NMR of which in deuterated chloroform-trifluoroacetic acid showed no bands for the protons at the ring junction. Broad multiplets at 8·5 (8 H), and 3·1 (4 H).

General procedure for the reduction of quinoxaline-di-N-*oxide to quinoxalines*

An excess of sodium dithionite in hot water was added in portions to a refluxing soln of the specific quinoxaline-di-N-oxide in 60% EtOH. On each addition, the yellow soln developed a red color that subsequently faded away. When the red coloration persisted for more that ½ hr, the addition of the sodium dithionite was discontinued. The soln was refluxed for an additional 3 hrs, cooled, diluted with water, and extracted with ether. The quinoxaline was obtained after the evaporation of the dried ether, and the product was recrystallized from MeOH.

Shorter reaction time resulted in the formation of quinoxaline mono-N-oxides which were purified by chromatography.

7,8,9,10-*Tetrahydro*-6H-*cyclohepta*[b]*quinoxaline* (VI, n = 5). 7,8,9,10-Tetrahydro-6*H*-cylohepta[*b*]quinoxaline-di-N-oxide (4·5 g) gave the title compound (3 g), m.p. 85–86° (lit.[13] 83·5–85°); IR: 1310, 1190, 1130, 955, 830, 760 cm^{-1}; NMR (CCl_4): broad singlet at 8·18 (6 H), multiplet at 6·86 (4 H), A_2B_2 system centered at 2·42 and 2·22 (2 H, 2 H). Mono-N-oxide derivative showed a broad singlet at 8·16 (6 H), multiplets at 6·84 (2 H) and 6·4 (2 H), and multiplets at 2·24 (3 H) and 1·6 (1 H).

6,7,8,9,10,11-*Hexahydrocycloocta*[b]*quinoxaline* (VI, n = 6). The title compound was obtained from the corresponding II(n = 6; 10 g). The product (8 g) melted at 122–123° (lit.[13] 120·2–120·7°); IR: 1305, 1160, 1140, 1120, 780 cm^{-1}; NMR (CCl_4): multiplets at 8·6 (4 H), 8·18 (4 H), and 6·86 (4 H), A_2B_2 system centred at 2·4 and 2·0 (2H, 2H).

7,8-*Dihydro*-6H-*cyclopenta*[b]*quinoxaline* (VI, n = 3). Was prepared from its di-N-oxide (II, n = 3; 6·3 g); yield 4·7 g. The product melted at 100–101° (lit.[14] 99–100°). IR: 1315, 1205, 1120, 780 cm^{-1}; NMR (CCl_4): multiplets at 7·75 (2 H) and 6·86 (4 H), A_2B_2 system centered at 2·35 and 2·13 (2H, 2H).

The reduction of quinoxalines with metallic sodium in absolute ethanol. The procedure followed was essentially that of Clemo and McIlwain.[6]

trans-5,5a,6,7,8,9,10,10a,11-*nonahydrocyclohepta*[b]*quinoxaline* (VII, n = 5). Compound VI(n = 5; 1 g) gave *trans*-5,5a,6,7,8,9,10,10a,11-nonahydrocyclohepta[*b*]quinoxaline (0·75 g). Recrystallization from light petroleum afforded plates that melted at 107–108°: IR: 3330 (doublet), 1600, 1300, 1260, 920, 910, 740 cm^{-1}; NMR: broad singlets at 8·4 (10 H), 6·6 (4 H), and 3·52 (4 H). (Found: C, 77·04; H, 8·89; N, 13·64. calc. for $C_{13}H_{18}N_2$: C, 77·18; H, 8·97; N, 13·85%).

trans-5,5a,6,7,8,9,10,11,11a,12-*Decahydrocycloocta*[b]*quinoxaline* (VII, n = 6). 6,7,8,9,10,11-Hexahydrocycloocta[*b*]quinoxaline (6 g) yielded the title compound (4 g). The product was recrystallized from light petroleum m.p. 97–98°; IR: 3310, 3280, 1600, 1295, 735 cm^{-1}; NMR: broad singlet at 8·3 (12 H), multiplet at 6·7 (4 H), and a singlet at 3·5 (4 H). (Found: C, 77·74; H, 9·34; N, 12·98. Calc. for $C_{14}H_{20}N_2$; C, 77·73; H, 9·32; N, 12·95%).

trans-5,5a,6,7,8,8a,9-*Heptahydrocyclopenta*[b]*quinoxaline* (VII, n = 3). 7,8-Dihydro-6H-cyclopenta[*b*]-quinoxaline yielded the title product after chromatography on a column of neutral alumina; recrystallization from MeOH gave m.p. 143–144°; IR: 3320, 3308, 1600, 1580, 1300, 922, 740, 700 cm^{-1}; NMR: multiplets at 8·1 (6 H) and 6·78 (2 H), singlets at 6·46 (2 H) and 3·38 (4 H). (Found: C, 75·61; H, 7·98; N, 16·23. Calc. for $C_{11}H_{14}N_2$: C, 75·82; H, 8·10; N, 16·08%).

TABLE 2

N,N'Diacetyl derivative	M.P.	IR (cm^{-1})	NMR[b]	UV λ max, mu	UV Σ × 10^{-4}
II, n = 3	150–151[a]	1640, 1280, 1100, 780	(m) 8·65 (4 H), (m) 8·9 (2 H), (s) 7·81 (6 H), (m) 4·6 (2 H), (s) 2·72 (4 H)	228 254 (sh)	3·94 2·1
II, n = 4	147[a]	1650, 1290, 1130, 1035, 980, 775, 765	(m) 8·6 (8 H), (s) 7·8 (6 H), (m) 5·15 (2 H), (s) 2·75 (4 H)	227 249 (sh)	4·89 2·69
d_2-II, n = 4	147[a]	1650, 1290, 1130, 1035, 980, 775, 765	(m) 8·58 (8 H), (s) 7·82 (6 H), (s) 2·8 (4 H)		
II, n = 5	162–163[c]	1650, 1500, 1320, 1290, 785	(m) 8·5 (10 H), (s) 7·86 (6 H), (m) 4·80 (2 H), (s) 2·70 (4 H)	226 245 (sh)	4·8 2·29
II, n = 6			(m) 8·46 (12 H), (s) 7·86 (6 H), (m) 4·91 (2 H), (s) 2·68 (4 H)	226 245 (sh)	4·8 2·3
VII, n = 4	182–183[a]	1670, 1600, 1430, 1320, 1300, 1260, 770	(m) 8·6 (8 H), (s) 7·81 (6 H), (m) 5·2 (2 H), (s) 2·73 (4 H)	226 248 (sh)	4·8 2·3
XII, n = 5	145–146[a]	1670, 1330, 780, 730	(m) 8·46 (12 H), (s) 7·85 (6 H), (m) 4·92 (2 H), (s) 2·70 (4 H)	224 249	4·5 2·6
XII, n = 6	186–188[c]	1650, 1320, 1290, 1250, 1070, 770	(m) 8·5 (10 H), (s) 7·86 (6 H), (m) 4·8 (2 H), (s) 2·69 (4 H)	223 248	4·6 2·5

[a] Recrystallized from petroleum ether-benzene
[b] In τ values
[c] Recrystallized from methanol
sh. Shoulder.

The N,N'-diacetyl derivatives of tetrahydroquinoxalines II and VII (n = 3,4,5,6) were prepared by treatment of the latter with pyridineacetic anhydride, either at room temp for 24 hr or by refluxing the soln for 2 hr. (Table 2).

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