The Reaction of *trans*-Decahydroquinoline with Molecular Oxygen [1]

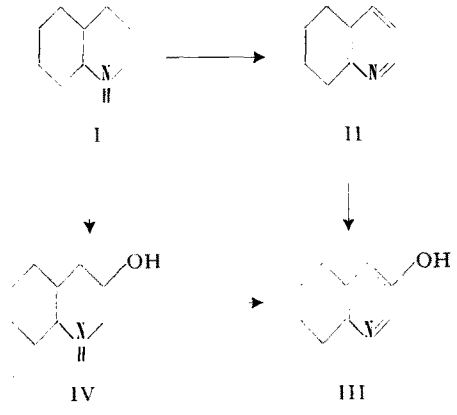
When a steady stream of oxygen was bubbled through *trans*-decahydroquinoline (m.p. 48°) at a temperature of 80–100° for a period of ten and more hours, no traces of peroxidic material were detectable at any time. In contrast to the oxygenation of *cis*-[2] and *trans*-decalin[3] any hydroperoxide initially formed in this case would probably be converted to the corresponding carbinol because of the secondary amino group present in the molecule[4].

The reaction mixture was separated into phenolic, basic and neutral fractions. The basic part consisted of starting material and 4–8% of a much weaker base, viz., 5,6,7,8-tetrahydroquinoline, isolated as the picrate, m.p. 158°[5]. Found: C, 49·67%; H, 3·93%; N, 15·64%. Calculated for $C_9H_{11}N{\cdot}C_6H_3N_3O_7$: C, 49·73%; H, 3·87%; N, 15·46%. Oxygen thus has effected a dehydrogenation of the heterocyclic moiety of the bicyclic system in accordance with the course of the dehydrogenation of *cis*- and *trans*-decahydroquinoline[6] and -isoquinoline[7]. The conversion of N-methylyohimbane to the cation of N-methyltetradehydroyohimbane by the action of catalytically excited oxygen at room temperature[8] is a related case.

The phenolic compound formed transparent prisms from ether, m.p. 198–200°. Found: C, 68·08%; H, 7·45%; N, 8·58% (compound dried at room temperature). Calculated for $C_9H_{11}NO{\cdot}1/2H_2O$: C, 68·33%; H, 7·65%; N, 8·85%. The picrate crystallized from methanol in tufts of yellow needles, m.p. 208–211°C. Found: C, 47·88%; H, 3·81%; N, 14·47%. Calculated for $C_9H_{11}NO{\cdot}C_6H_3N_3O_7$: C, 47·62%; H, 3·73%; N, 14·81%.

The composition, the phenolic character and the similarity of the ultraviolet absorption data with those of 3-hydroxypyridine[9] (Table) suggest the structure of the hitherto unknown 3-hydroxy-5,6,7,8-tetrahydroquinoline (III). The *bathochromic* shift observed in the ultraviolet spectrum on the formation of the anion (or cation) is typical of phenolic compounds and rules out the analogous 2- and 4-tetrahydroquinolones which would show a *hypsochromic* shift[1].

The neutral fraction contained at least two different compounds so far not obtained crystalline but characterized by infrared data. The fraction more easily eluted from Al_2O_3 by benzene containing 1% chloroform showed (in $CHCl_3$) carbonyl bands at 5·84 and 6·15 μ. The subsequent fraction, distillable at 170°/0·3 mm showed (in $CHCl_3$) a weak band at 2·94 (>NH), a sharp and strong band at 6·05 and 6·90 (>CO-NH), indicating a compound possibly related to the known 5,6,7,8-tetrahydro-[2] or *trans*-octahydrocarbostyril[3], excluding carbostyril (bands at 3·0; 6·06[s]; 6·24[m]; 6·44[m]; no band at 6·90) and 1,2,3,4-tetrahydrocarbostyril (2·98; 5·99[s]; 6·30[s]; 6·80[s]). However, the absence of secondary amide bands in the 6·5 μ region more or less eliminates any (hydrogenated) carbostyril structures; the two neutral fractions are rather the products of a complicated sequence of oxidation and rearrangement reactions to be reported elsewhere (ref. [4]).



The phenolic 3-hydroxy-5,6,7,8-tetrahydroquinoline (III) is probably formed by further oxidation of the parent II rather than by dehydrogenation of the hypo-

[1] Oxidation Mechanisms. XIV. Preceding paper: B. WITKOP and S. GOODWIN, J. Amer. Chem. Soc. *76*, 1954, in press.

[2] R. CRIEGEE, Ber. dtsch. chem. Ges. *77*, 22, 722 (1944).

[3] H. KLEINFELLER and C. ODEFEY, Angew. Chem. *62*, 342 (1950).

[4] *Cf.* C. W. CAPP and E. G. E. HAWKINS, J. Chem. Soc. *1953*, 4106.

[5] M. EHRENSTEIN and W. BUNGE, Ber. dtsch. chem. Ges. *67*, 1715 (1934).

[6] J. v. BRAUN and G. LEMKE, Liebigs Ann. Chem. *478*, 191 (1930). – M. EHRENSTEIN and W. BUNGE, Ber. dtsch. chem. Ges. *67*, 1715 (1934).

[7] B. WITKOP, J. Amer. Chem. Soc. *70*, 2617 (1948).

[8] B. WITKOP, J. Amer. Chem. Soc. *75*, 3361 (1953).

[9] H. SPECKER and H. GAWROSCH, Ber. dtsch. chem. Ges. *75*, 1347 (1942). – *Cf.* T. R. GOVINDACHARI and N. S. NARASIMHAN, J. Chem. Soc. *1953*, 2635.

[1] H. SPECKER and H. GAWROSCH, Ber. dtsch. chem. Ges. *75*, 1347 (1942). – *Cf.* T. R. GOVINDACHARI and N. S. NARASIMHAN, J. Chem. Soc. *1953* 2635.

[2] H. K. SEN-GUPTA J. Chem. Soc. *107*, 1357 (1915); *cf.* A. DORNOW and E. NEUSE, Ber. dtsch. chem. Ges. *84*, 296 (1951).

[3] W. HÜCKEL and F. STEPF, Liebigs Ann. Chem. *453* 168 (1927).

[4] L. A. COHEN and B. WITKOP, J. Amer. Chem. Soc. (in prep.)

Solvent	Phenolic Oxidation Product of *trans*-Decahydroquinoline		Solvent	3-Hydroxypyridine[1]	
	λmax (log ε)	$\Delta\lambda$		λmax (log ε)	$\Delta\lambda$
EtOH	292 (3·71)	–	MeOH	277 (3·61)	–
0·1*N*-HCl-EtOH	303 (3·84)	+11	0·1*N*-HCl-MeOH	284 (3·81)	+ 7
0·1*N*-KOH-EtOH	315 (3·72)	+22	0·1*N*-KOH-MeOH	301 (3·62)	+24

Absorption maxima of the phenolic oxidation product from I and of 3-hydroxypyridine; $\Delta\lambda$ signifies the bathochromic shift when going from the free base (or zwitterion) to the cation or anion.

[1] H. SPECKER and H. GAWROSCH, Ber. dtsch. chem. Ges. *75*, 1347 (1942). – *Cf.* T. R. GOVINDACHARI and N. S. NARASIMHAN, J. Chem. Soc. *1953*, 2635.

thetical 3-hydroxydecahydroquinoline (IV). The former course of oxidation is analogous to the introduction of β-hydroxy groups into pyridine[1] and quinoline[2] on biological oxidation. The latter route would be comparable to the β-oxygenation of *trans*-decaline (→ β-decalone)[3]. The possible introduction of a hydroxy group in the 2-position is reminiscent of the oxidation of niacine[4] and quinine[5].

By contrast, $\Delta^{1(9)}$-octahydroquinoline, being a tertiary unsaturated amine with only one activated tertiary center for the attack of oxygen, easily forms, as do similar bicyclic systems of this type a beautifully crystalline hydroperoxide[6].

B. WITKOP

National Institutes of Health, Washington 14, D.C., April 21, 1954.

Zusammenfassung

Dem phenolischen Oxydationsprodukt, das beim Durchleiten von Sauerstoff durch geschmolzenes *trans*-Dekahydrochinolin entsteht, wird auf Grund der Analyse und spektrophotometrischen Daten die Konstitution III eines 3-Oxy-5, 6, 7, 8-tetrahydrochinolins beigelegt. Seine Entstehung erfolgt wahrscheinlich über das gleichfalls gebildete 5, 6, 7, 8-Tetrahydrochinolin.

[1] *Cf.* J. N. SMITH and R. T. WILLIAMS, Biochem. J. *56*, 325 (1954).
[2] L. NOVACK and B. B. BRODIE, J. Biol. Chem. *187*, 787 (1950).
[3] H. KLEINFELLER and C. ODEFEY, Angew. Chem. *62*, 342 (1950).
[4] *Cf.* M. E. PULLMAN and S. P. COLOWICK, J. Biol. Chem. *206*, 121 (1954).
[5] B. B. BRODIE, J. E. BAER, and L. C. CRAIG, J. Biol. Chem. *188*, 567 (1951).
[6] L. A. COHEN and B. WITKOP, J. Amer. Chem. Soc. (in preparation).

Spectrophotometric Differences between Aminoheterocyclic Bases and Their Salts

When an open or cyclic base of the SCHIFF type containing the element >C=N– passes into the cation >C=$\overset{\oplus}{\text{N}}$H– three major spectroscopic changes are observed in the ultraviolet and infrared absorption spectra:

(1) A bathochromic shift in the ultraviolet ranging between 1 and 50 mμ and more depending on the type of compound and the presence of auxochromic groups[1]. A hypsochromic shift on salt formation usually indicates the participation of the cation >C=$\overset{\oplus}{\text{N}}$H– in partial or complete *intra-* or *inter*molecular addition reactions[2]. Pyridine and its derivatives are not normally looked upon as cyclic SCHIFF bases, although a number of chemical reactions (1, 2-addition and reduction, such as addition of alkyl lithium, HAMMICK reaction, acyloin-like condensations with aldehydes, etc.) clearly indicate the independence of the "ammono-aldehyde" (MORTON) system. In other respects pyridine exhibits aromatic character. This dualistic behavior is reflected in the effect of salt formation on the ultraviolet absorption of pyridines which may vary from hypsochromic to bathochromic (Table I).

[1] *Cf.* B. WITKOP, J. B. PATRICK, and H. M. KISSMAN, Ber. dtsch. chem. Ges. *85*, 949 (1952).
[2] *Cf.* E. D. BERGMANN, Chem. Rev. *53*, 309 (1953).

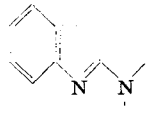
Table I

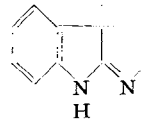
Influence of Salt Formation on the Ultraviolet Absorption of Some Pyridines (solvent ethanol if not stated otherwise).

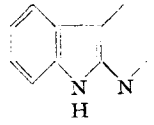
	λ_{max} free base	λ_{max} salt	$\Delta\lambda$
Pyridoxamine	308 (3·86)[a]	293 (3·95)	–15
Pyridoxal	300 (3·76)	288 (3·93)	–12
Pyridine[b]	257 (3·43)[c]	256 (3·73)	– 1
Nicotine[b]	262 (3·46)	260 (3·68)	– 2
2,6-Lutidine[b]	267 (3·48)[d]	272 (3·68)	+ 5
3-Vinylpyridine[b]	278 (3·44)	287 (3·53)	+ 9
Nicotyrine[b]	288 (3·99)	310 (4·04)	+22

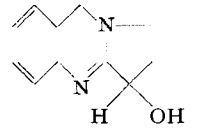
[a] Measured in 0·1 *N* NaOH: A. MEISTER, E. A. PETERSON, and H. A. SOBER, J. Amer. Chem. Soc. *76*, 169 (1954). [b] M. L. SWAIN, A. EISNER, C. F. WOODWARD, and B. A. BRICE, J. Amer. Chem. Soc. *71*, 1341 (1949), measured in 95% alcohol. [c] *Cf.* H. V. DAENIKER, Helv. chim. Acta *35*, 1955 (1952). [d] Measured in isooctane: R. A. FRIEDEL and M. ORCHIN, *Ultraviolet Spectra of Aromatic Compounds* (John Willey and Sons, Inc., New York, 1951), p. 106. – F. G. HERINGTON, Discussions of the Faraday Society *9*, 26 (1950).

α- and γ-aminopyridines are no longer formulated as α- or γ-pyridone imines but as cyclic (vinylogous) amidines; the true N-methyl pyridone imines which are only present in anhydrous inert solvents, absorb at much longer wave length than their tautomeric amidine cations; in this respect the salt formation has a hypsochromic effect. A slight hypsochromic effect is also observed when forming the salt of α-aminoindolenine, the properties of which (Table III) are best explained by formula I rather than II[1] or III[2], or of a cyclic amidine where the amino group forms part of a second ring as in vasicine (peganine, IV, Table III).


I


II


III


IV

(2) The infrared absorption of the >C=N– group (6·10–6·15 in aromatic SCHIFF bases, 6·24–6·28 in pyridines[3]) on salt formation invariably moves to shorter wave length (5·98–6·08 in SCHIFF bases, 6·07–6·13 in pyridines). This hypsochromic shift is even stronger in open and cyclic amidines (Table II and III) and clearly

[1] H. RINDERKNECHT, H. KOECHLIN, and C. NIEMANN, J. Org. Chem. *18*, 971 (1953).
[2] R. PSCHORR and G. HOPPE, Ber. dtsch. chem. Ges. *43*, 2543 (1910).
[3] The assignment of the band 6·28μ (1590 cm^{-1}) to the group >C=N– in pyridines (H. M. RANDALL, R. G. FOWLER, N. FUSON, and J. R. DANGL, *Infrared Determination of Organic Structures* [D. Van Nostrand Co., New York, 1949], p. 32) or pyrimidines (*Cf.* I. A. BROWNLIE, J. Chem. Soc. *1950* 3062), or other heterocycles is a simplification convenient for the purpose of comparison with the hydrochlorides. Normally no absolute assignments to >C=C< or >C=N– in conjugated systems can be made with certainty (*Cf.* E. R. BLOUT, M. FIELDS, and R. KARPLUS, J. Amer. Chem. Soc. *70*, 194 [1948]).