recognized that *only infrequently* do phenyl groups give analyzable NSR patterns. *Para*-substituents having spin $^1/_2$ (F^{19}, P^{31}) introduce some complexity and should be avoided; all others (including D) appear quite satisfactory.

A further advantage is gained in the present instance by the use of "*para*-sensitive" groups such as methyl and methoxy (formyl, acetyl, and dimethylamino also are good) which give sharp NSR peaks, the exact spectral location of which is dependent upon the electrical nature of the structure attached *para* to them.[9] Thus, the 3-position in the formazan appears to be slightly electron-withdrawing, the methoxy shift being −0.048 p.p.m. relative to anisole,[10] while the *average* of the 1- and 5- positions is slightly electron-donating as judged by the positive methyl shift, +0.021 p.p.m., compared to toluene.[10]

The two apparently different *p*-tolyl groups of I in fact yield identical spectral patterns; if a symmetrical, "mesomeric" structure be ruled out, the observed equivalence requires rapid tautomerization, with an estimated lower limit for the rate constant being *ca.* 10^3 sec.$^{-1}$.[8] An alternative explanation, based on rapid intermolecular NH exchange, is excluded, as it would require a sharp NH peak (not seen), the effects of spin-spin interaction and quadrupole broadening by N^{14} being averaged to zero by such exchange.[11]

EXPERIMENTAL

The NSR equipment and techniques used were previously described.[10,12]

1,5-Di-(4-methylphenyl)-3-(4-methoxyphenyl)-formazan (I). A solution of 2.4 g. (0.01 mol.) of *p*-anisaldehyde-*p*-tolylhydrazone in 300 ml. 95% ethanol at 0° was treated with a diazonium salt solution prepared from 1.07 g. (0.01 mol.) *p*-toluidine, 2.5 ml. (0.03 mol.) 12*N* HCl and 0.76 g. (0.11 mol.) sodium nitrite, at 0°. The *p*H of the diazonium salt solution was adjusted to 6.5 by means of sodium acetate, and it was added dropwise to the vigorously stirred hydrazone solution. After 15 min. a yellow solid was filtered from the solution and allowed to stand until its color was deep red; it was twice recrystallized from ethanol, 2.6 g. (73%) being recovered as deep red needles, m p. 172–175° (uncorr.).

Anal. Calcd. for $C_{22}H_{22}ON_4$: N, 15.64%. Found: N, 16.08%.

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CHEMISTRY DEPT.
KANSAS STATE UNIV.
MANHATTAN, KAN.
CENTRAL RESEARCH DEPT.
MINN. MINING & MFG. CO.
ST. PAUL 9, MINN.

(9) G. V. D. Tiers, Presented at the Symposium on Nuclear Resonance Spectroscopy, Joint SAS-ASTM E-13 Meeting, New York, 1958.

(10) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(11) Ref. 8, p. 102 and p. 226.

(12) G. V. D. Tiers and F. A. Bovey, *J. Phys. Chem.*, **63**, 302 (1959).

The Tetrazole-Azidoazomethine Equilibrium. III. Reduction of Pyridotetrazoles[1]

J. H. BOYER, M. S. CHANG, AND R. F. REINISCH

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The presence of an equilibrium between pyridotetrazole (I) and 2-azidopyridine (III) with electron withdrawing substituents in the pyridine ring was established by spectrophotometric detection of both azido and tetrazolo groups in solutions of certain examples. With no substituent or with electron donating substituents, azide concentration, if present, was not detected.[2] The marked stability of pyridotetrazole in strong acid[3] may be explained by an electromeric displacement toward the electron seeking tetrazole ring. An electromeric displacement toward the pyridine ring, on the other hand, would decrease the stability of the tetrazole ring in I relative to its tautomer III, and might be realized in alkaline solutions.[4] A confirmation of the two possible electronic displacements has been found in catalytic hydrogenation of pyridotetrazole in acidic, basic and neutral media and by reduction of 7-methyl-8-nitropyridotetrazole with stannous chloride in hydrochloric acid.

A detailed catalytic reduction of the tetrazole ring has not been reported heretofore.[5] Its resistance to catalytic hydrogenation was demonstrated in the reduction of I over a noble metal to di- and tetrahydropyridotetrazole[6] (II) and in the reduction of 5-phenyltetrazole in acetic acid over platinum to 5-cyclohexyltetrazole.[7] In the present work, reduction of pyridotetrazole (I) over palladium in the presence of acetic acid to tetramethylenetetrazole (II) in nearly quantitative yield, together with a trace of 2-aminopyridine (IV) has been realized. A dihydropyridotetrazole is not detected. In con-

(1) Financial support by E. Bilhuber, Inc., Orange, New Jersey, and by Research Grants H-2295 and CY-2895 from the National Institutes of Health is gratefully acknowledged.

(2) J. H. Boyer and E. J. Miller, Jr., *J. Am. Chem. Soc.*, **81**, 4671 (1959) (Part I); J. H. Boyer and H. W Hyde, *J. Org. Chem.*, in press.

(3) Pyridotetrazole is recovered unchanged from concentrated sulfuric acid at 120° (J. H. Boyer, W. J. McCarville, D. I. McCane, and A. T. Tweedie, *J. Am. Chem. Soc.*, **75**, 5298 (1953).

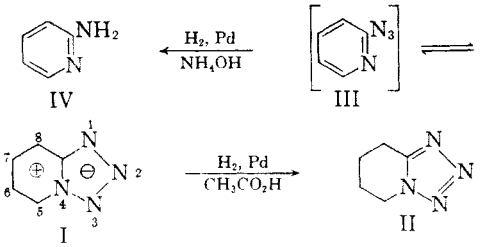
(4) Preliminary observations suggested an instability of pyridotetrazole and its derivatives in bases.[3]

(5) Ring cleavage of tetrazolium salts may occur upon catalytic reduction over palladium [D. Jerchel and R. Kuhn, *Ann.*, **568**, 185 (1950)]. R. O. Roblin, Jr., J. H. Williams, P. S. Winnek, and J. P. English, *J. Org. Chem.*, **62**, 2002 (1940) state that 5-*p*-nitrobenzenesulfonamidotetrazole is reduced over palladium to sulfanilylguanidine, but they do not give the experimental procedure.

(6) Kereszty and Wolf, German pat. **613,123** [*C. A.* **29**, 5604 (1935)]; U. S. pat. **2,008,536** [*C. A.* **29**, 5994 (1935)]. The solvent is not specified in the abstracts.

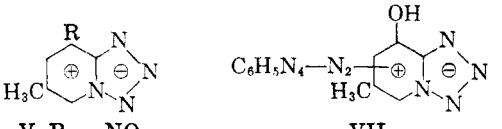
(7) B. Elpern and F. C. Nachod, *J. Am. Chem. Soc.*, **72**, 3379 (1950).

trast, reduction in the presence of ammonium hydroxide gives 2-aminopyridine (IV) inm oderate yield with no tetramethylenetetrazole and a similar reduction in ethanol gives lower yields of both II and IV.



Stannous chloride in hydrochloric acid transforms 6-methyl-8-nitropyridotetrazole (V) into 6-methyl-8-aminopyridotetrazole (VI). Apparently tetrazole destabilization as a result of the presence of the electron attracting nitro group is ineffective in the presence of an opposing electromeric shift demanded by the acid environment.

A derivative tentatively assigned the structure of an azo compound (VII) is obtained upon treatment of diazotized VI with boiling water.



V, R = NO_2
VI, R = NH_2

VII

EXPERIMENTAL[8]

Tetramethylenetetrazole. A solution of 10.65 g. (0.09 mol.) of pyridotetrazole in 5.40 g. (0.09 mol.) of glacial acetic acid and 200 ml. of 95% ethanol was treated with hydrogen (initial pressure of 2 atm.) over 1.25 g. of 10% palladium on charcoal. Hydrogen pressure decreased to a constant value after about 4 hr. The solution, separated from catalyst, was evaporated to dryness *in vacuo*. Addition of *n*-hexane to dried and decolorized chloroform extracts of the residue precipitated 8.6 g. (85%) of tetramethylenetetrazole as colorless needles, m.p. 117–118° after recrystallization from a mixture of chloroform and *n*-hexane (lit.[9] m.p. 115–116°).

Anal. Calcd. for $C_5H_8N_4$: C, 48.38; H, 6.49; N, 45.14. Found: C, 48.65; H, 6.54; N, 45.39.

A trace of 2-aminopyridine in the filtrate was detected as the picrate, melting point and mixture melting point 215–216° (lit.[9] m.p. 216–217°).

The reduction was repeated with the substitution of 0.09 mol. of ammonium hydroxide for 0.09 mol. of glacial acetic acid. Addition of hexane to a chloroform solution of the product did not precipitate tetramethylenetetrazole. Addition of a saturated ethanolic solution of picric acid gave 7.81 g. of *2-aminopyridine* picrate, melting point and mixture melting point 216–217° after recrystallization. Based upon quantitative picrate formation this represents a 29.4% yield of 2-aminopyridine.

In another reduction, neither acid nor base was added to the ethanol solvent. A 15.8% yield of 2-aminopyridine was isolated as its picrate derivative and a 35.0% yield of tetramethylenetetrazole was obtained.

Preparation of 6-methyl-8-aminopyridotetrazole. A solution of 11.3 g. (0.05 mol.) of stannous chloride dihydrate and 15 ml. of concentrated hydrochloric acid was cooled to 5°. The temperature rose to about 60° with the addition of 1.69 g. (0.01 mol.) of 6-methyl-8-nitropyridotetrazole[10] in one portion. The solution was vigorously stirred for about 5 min. until a clear solution resulted and was then stirred in an ice bath for 1 hr. and filtered. The filtrate was treated dropwise with a solution of 40% sodium hydroxide to precipitate the amine as a fine solid, 0.92 g. (61%), m.p. 214–215° (dec.) after recrystallization from boiling water and drying *in vacuo* overnight at 80°.

Anal. Calcd. for $C_6H_7N_5$: C, 48.31; H, 4.73; N, 46.95. Found: C, 48.43; H, 4.90; N, 46.86.

Preparation of 6-methyl-8-acetamidopyridotetrazole. A solution of 0.3 g. (0.002 mol.) of 6-methyl-8-aminopyridotetrazole and 2 g. of acetic anhydride was heated for a few minutes, and cooled. The precipitate, 0.32 g. (84%), m.p. 238–239°, was recrystallized from ethanol.

Anal. Calcd. for $C_8H_9N_5O$: C, 50.25; H, 4.74; N, 36.63; O, 8.37. Found: C, 50.45; H, 4.72; N, 36.83; O, 8.53.

Preparation of 6-methyl-8-hydroxy 5(or 7)-(8′-azo-6′-methyl-pyridotetrazolo)-pyridotetrazole. A solution of 0.3 g. (0.002 mol.) of 6-methyl-8-aminopyridotetrazole, 3 g. of water and 3.6 g. (0.36 mol.) of concentrated sulfuric acid was chilled to 0–5° in an ice-salt bath with stirring. Dropwise addition of a solution of 0.15 g. (0.0022 mol.) of sodium nitrite was accompanied by an evolution of gas. After stirring for 5 to 10 min. the diazotization mixture was added slowly to 10–20 ml. of boiling water. A crude red solid after recrystallization from *N,N*-dimethylformamide gave 0.05 g. (48.4%) of 6-methyl-8-hydroxy 5(or 7)-8′-azo-6′-methyl-pyridotetrazole)-pyridotetrazole, m.p. 230° (explosive dec.) and 0.20 g. of starting material, m.p. 214–215°.

Anal. Calcd. for $C_{12}H_{10}N_{10}O$: C, 46.49; H, 3.25; N, 45.18; O, 5.16. Found: C, 46.70; H, 3.29; N, 44.61; O, 5.87.

CHEMISTRY DEPARTMENT
TULANE UNIVERSITY
NEW ORLEANS 18, LOUISIANA

(8) Semimicro analyses by Alfred Bernhardt, Max Planck Institut Mülheim (Ruhr), Germany. Melting points are not corrected.

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Hofmann Degradation of 3a-(3,4-Methylenedioxyphenyl)-1-methyloctahydroindole

P. F. HIGHET AND W. C. WILDMAN

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The synthesis of (±)-crinane (III) demonstrated that several Amaryllidaceae alkaloids are derivatives of 5,10b-ethanophenanthridine.[1,2] A key intermediate in this synthesis was the hexahydroindole (I) which was reduced by catalytic methods to an octahydroindole of unknown stereochemistry. It was reasoned[3] that catalytic hydrogenation of I should proceed by the addition of hydrogen to the enamine from the side opposite that occupied

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(3) N. Sugimoto and H. Kugita, *Pharm. Bull.*, **5**, 378 (1957).