TABLE I[a]

N-ALKYLNAPHTHALIMIDES

N-Alkyl Substituent	Yield,[b] %	M.P.	Solvent[c]	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Methyl	92	206.5[d]	A	$C_{13}H_9NO_2$		
Ethyl	88	154[e]	A	$C_{14}H_{11}NO_2$		
Propyl	90	158–159	B	$C_{15}H_{13}NO_2$	5.86	6.14
Isopropyl	12	163–164	C	$C_{15}H_{13}NO_2$	5.86	5.63
Butyl	95	96.5–97	B	$C_{16}H_{15}NO_2$	5.53	5.27
sec-Butyl	4	111–112	C	$C_{16}H_{15}NO_2$	5.53	5.43
Amyl	55	86	C	$C_{17}H_{17}NO_2$	5.24	5.10
Isoamyl	57	104–105	C	$C_{17}H_{17}NO_2$	5.24	5.11
1-Methylbutyl	4	69	D	$C_{17}H_{17}NO_2$	5.24	5.50
Hexyl	75	81.5–82.5	B	$C_{18}H_{19}NO_2$	4.97	5.24
Heptyl	90	70.5–71.5	C	$C_{19}H_{21}NO_2$	4.74	4.79
Octyl	43	42.5–43.5	A	$C_{20}H_{23}NO_2$	4.52	4.50
Nonyl	95	56.5–57	C	$C_{21}H_{25}NO_2$	4.33	4.01
Decyl	95	52	A	$C_{22}H_{27}NO_2$	4.19	4.29
Undecyl	80	53–53.5	C	$C_{23}H_{29}NO_2$	3.98	3.99
Dodecyl	95	56–57	E	$C_{24}H_{31}NO_2$	3.83	3.85
Benzyl	82	95–96	B	$C_{19}H_{13}NO_2$	4.87	5.01

[a] All melting points are corrected. [b] Crude yield based on potassium naphthalimide. [c] Recrystallizing solvent: A = .95% ethanol; B = isopropanol; C = isopropanol-water; D = methanol-water; E = methanol. [d] G. F. Jaubert, *Ber.*, **28**, 360 (1895) reported m.p. 205°. [e] G. F. Jaubert, *op. cit.*, reported m.p. 148°.

EXPERIMENTAL

N-Alkylnaphthalimides. In a small flask fitted with an efficient reflux condenser were placed 2.35 g. (0.01 mol.) of potassium naphthalimide,[8] the appropriate alkyl halide (0.01 mol.), and 15 ml. of dimethyl formamide. The mixture was refluxed on a steam bath for 1 hr. and cooled, and the precipitated potassium bromide was removed by filtration. Cold water was added to the filtrate and the precipitated *N*-alkyl naphthalimide was removed and dissolved in ether. Any ether insoluble material was removed and the ether evaporated to give the crude product which was recrystallized.

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(8) A. M. Mattocks and O. S. Hutchinson, *J. Am. Chem. Soc.*, **70**, 3474 (1948).

Tetrazole-Azidoazomethine Equilibrium. II. Amino- and Hydroxypyridotetrazoles[1]

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TABLE I

INFRARED ABSORPTION (cm.$^{-1}$) FROM KBr DISKS (% TRANSMITTANCE)

8-Amino-pyridotetrazole (I)	8-Hydroxy-pyridotetrazole (II)	6-Hydroxy-pyridotetrazole (III)
3401 (35.0)	3059 (18.0)	3448 (51.8)
3300 (32.5)	2994 (18.2)	2564 (27.0)
3195 (34.9)	2793 (25.6)	1923 (51.7)
3096 (39.6)	2660 (24.0)	1786 (55.6)
1639 (30.5)	2475 (40.0)	1656 (48.0)
1570 (39.3)	1894 (74.8)	1570 (49.4)
1497 (36.9)	1835 (79.2)	1553 (40.7)
1414 (42.6)	1764 (78.6)	1515 (28.5)
1381 (43.2)	1631 (34.5)	1431 (23.7)
1361 (45.0)	1585 (6.5)	1350 (29.0)
1318 (48.6)	1502 (18.9)	1311 (23.7)
1232 (56.5)	1429 (15.7)	1259 (37.6)
1220 (37.7)	1393 (30.0)	1211 (24.0)
1156 (40.7)	1321 (15.0)	1147 (37.7)
1107 (40.0)	1239 (28.9)	1106 (23.0)
1076 (36.5)	1206 (21.0)	1095 (25.3)
1067 (42.9)	1159 (14.0)	1028 (41.5)
938 (50.0)	1104 (34.3)	964 (49.0)
841 (39.0)	1067 (45.4)	873 (27.6)
716 (28.0)	1044 (47.2)	815 (19.4)
701 (46.5)	1016 (24.6)	793 (26.5)
693 (47.4)	952 (71.0)	768 (32.4)
	880 (44.5)	696 (46.4)
	849 (68.7)	
	794 (44.0)	
	774 (26.0)	
	744 (21.3)	
	696 (30.0)	

The predicted absence[2] of tetrazole-azidoazomethine tautomerism for derivatives of pyridotetrazole with certain strong electron donating substituents has been established by examination of 6- and 8-hydroxy- and 8-aminopyridotetrazole. On treatment with sodium azide in the presence of hydrochloric acid in refluxing aqueous ethanol, 2-chloro-3-amino- and 2-chloro-3-hydroxypyridine are transformed into 8-amino- (I) and 8-hydroxypyridotetrazole (II) respectively. A similar reaction with 2-chloro-5-aminopyridine occurs with the unexpected replacement of the amino group with the hydroxyl group. It is assumed that the functional group has not migrated to another position

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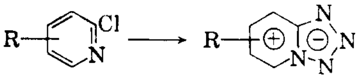
TABLE II

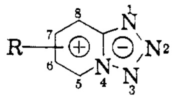
PREPARATION OF PYRIDOTETRAZOLES FROM 2-CHLOROPYRIDINES



Chloro-pyridine R	Pyrido-tetrazole R	M.P. (dec.)	Yield, %	Molecular Formula	Analysis Carbon, % Calcd. Found	Analysis Nitrogen, % Calcd. Found	Analysis Nitrogen, % Calcd. Found
3-NH_2	8-NH_2 (I)[a]	180–183	32[b]	$C_5H_5N_4$	44.43	3.73	51.86
					44.34	3.86	52.30
3-$N(COCH_3)_2$[c]	8-$NHCOCH_3$	207–210[d]	3[e]	$C_7H_7N_5O$	47.45	3.99	39.74
					47.66	4.22	39.23
3-OH[c]	8-OH (II)[a,f]	>220	22	$C_5H_4N_4O$	44.11	2.95	41.26
					44.18	3.15	41.40
5-NH_2	6-OH (III)[a]	215–220	19[h]	$C_5H_4N_4O$	44.11	2.95	41.26
					44.39	3.01	40.70

[a] Samples in ethanol gave ultraviolet absorption recorded by a Beckman Quartz Spectrophotometer, Model DK. [b] Based on 70% recovery of starting material. [c] Ref. 6. [d] Also obtained for the product from I and acetic anhydride. [e] Based on the transformation of 55% starting material into 2-chloro-3-acetamidopyridine. [f] From 8.5 g. (0.066 mol.) of 2-chloro-3-pyridinol, m.p. 164–165°, II is obtained in 22% yield with 4.4 g. of an unidentified product, m.p. 184–186° (dec.). *Anal.* Found: C, 46.26; H, 3.38; N, 12.34. [g] A. Binz and O. v. Schickh, *Ber.*, **68**, 315 (1935). [h] Based on 50% recovery of starting material.

and that the product is 6-hydroxypyridotetrazole (III).



I. R = 8-NH_2
II. R = 8-OH
III. R = 6-OH

Similar attempts to obtain the other five unknown hydroxy- and aminopyridotetrazoles from corresponding halopyridines have been unsuccessful. Halogen in 2-bromo-4-nitropyridine, 2-chloro-3-acetamidopyridine, 2-bromo-4-aminopyridine and 2-bromo-6-aminopyridine resists displacement by the azido group in acid solutions of hydrogen azide. Chlorine in 2-chloro-3-acetamidopyridine is unreactive to silver azide and in 2-chloro-3-aminopyridine is unreactive to hydrazine.

Infrared absorption (Table I) in the region 1100 to 1000 cm.$^{-1}$ for I (three bands), II (four bands) and III (three bands) in potassium bromide disks may be characteristic of the tetrazole ring;[3] however, absorption in the region 770 to 730 cm.$^{-1}$ in which tetrazole absorption has been found,[3] is less consistent.

Since each of the three compounds is transparent in the region 2160–2120 cm.$^{-1}$ [2] in either potassium bromide disks or *N*,*N*-dimethylformamide solution it is concluded that tautomeric azide structures are not present in either the solid state or in certain solutions.

Ultraviolet absorption for 8-aminopyridotetrazole in ethanol at 288 mμ (log ϵ 3.17) and for 8-hydroxypyridotetrazole in ethanol at 270 mμ (log ϵ 3.70) represents expected bathochromic shifts from absorption at 260 mμ (log ϵ 3.72) for pyridotetrazole in ethanol. Two bands for 6-hydroxypyridotetrazole in ethanol, one at 292 mμ (log ϵ 2.49) the other at 260 mμ (log ϵ 2.50), are assigned to the tetrazole (III) rather than tautomeric 2-azido-5-hydroxypyridine[4] in agreement with its lack of infrared absorption in the region 2160 to 2120 cm.$^{-1}$

EXPERIMENTAL[5]

8-Aminopyridotetrazole. A solution of 1.0 g. (0.009 mol.) of 3-amino-2-chloropyridine m.p. 80–81°,[6] 40 ml. of ethanol, and 10 ml. of water was added to a solution of 1.0 g. (0.016 mol.) of sodium azide, 7 ml. of ethanol, and 15 ml. of water. After addition of 5.0 ml. (0.024 mol.) and 4.8*N* hydrochloric acid, the solution was refluxed for 96 hr. and evaporated to bring about precipitation of a solid which recrystallized from benzene as colorless needles, m.p. 180–183° (dec.), 0.10 g. (32%, based on recovered 3-amino-2-chloropyridine). Repeated recrystallization raised the melting point to 184–185° (dec.). Neutralization of the original filtrate gave 0.7 g. of crude 3-amino-2-chloropyridine, m.p. 77–79°. Analytical data and other similar preparations are described in Table II.

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[2] J. H. Boyer and E. J. Miller, Jr., *J. Am. Chem. Soc.*, **81**, 4671 (1959).

[3] E. Lieber, D. Levering, and L. Patterson, *Anal. Chem.*, **23**, 1594 (1951) report that tetrazoles absorb between 1100 and 1000 cm.$^{-1}$ where up to three bands may occur and in the 763 to 758 cm.$^{-1}$ and 741 to 735 cm.$^{-1}$ regions.

[4] Absorption at 285 mμ (log ϵ 2.1) has been reported for phenyl azide in ethanol (yu. N. Sheĭnker and M. V. Lomonosar, *Doklady Akad. Nauk S.S.S.R.*, **77**, 1043 (1951). *Chem. Abstr.*, **45**, 6927 (1951).

[5] Semimicro analyses by Alfred Bernhardt, Max Planck Institut Mülheim (Ruhr), Germany. Melting points are uncorrected.

[6] O. v. Schickh, A. Binz, and A. Schulz, *Ber.*, **69**, 2593 (1936).