Investigation of Some Tetrazole Derivatives of 1,8-Naphthyridines

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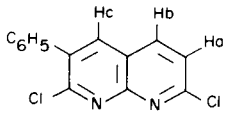
Several tetrazole derivatives have been prepared from 7-amino-2-hydroxy-3-phenyl-1,8-naphthyridine (Id). Evidence is presented to demonstrate that the tetrazole ring structure is the dominant species in the solid state and in alkaline solution while the open-chain azido form dominates in acidic solution. In addition it has been shown that the presence of a phenyl group in a position adjacent to the tetrazole nucleus apparently stabilizes the tetrazole ring.

In the course of our studies on 1,8-naphthyridine derivatives, a product, to which the structure of 7-amino-2-hydroxy-3-phenyl-1,8-naphthyridine (Id) was suggested, was prepared by the reaction of ethyl phenylformylacetate with 2,6-diaminopyridine in concentrated sulfuric acid (1). This structural assignment has now been confirmed by the transformation of Id into 8-acetylamino-4-phenyltetrazolo[1,5-*a*][1,8]naphthyridine (VId) (see Scheme I) and the oxidation of the latter compound to tetrazole and 5-benzoyltetrazole (see Experimental) (2). Compound VId was obtained from 7-amino-2-hydroxy-3-phenyl-1,8-naphthyridine (Id), through the acetyl derivatives IVd, acetylaminochloronaphthyridine VIId and by reaction of this latter with sodium azide. The structure of 8-acetylamino-4-phenyltetrazolo[1,5-*a*][1,8]naphthyridine (VId) was also supported by IR spectral data (see Table IV). The structural assignment of Id was confirmed by NMR spectrum of the dichloro derivative IIId, which was prepared by treatment of Id with nitrous acid to give IId, followed by the reaction with phosphorus oxychloride. It was impossible to obtain the NMR spectrum of Id because of its insolubility.

NMR Spectral Data of 2,7-Dichloro-3-phenyl-1,8-naphthyridine (IIId) in DMSO-d_6.

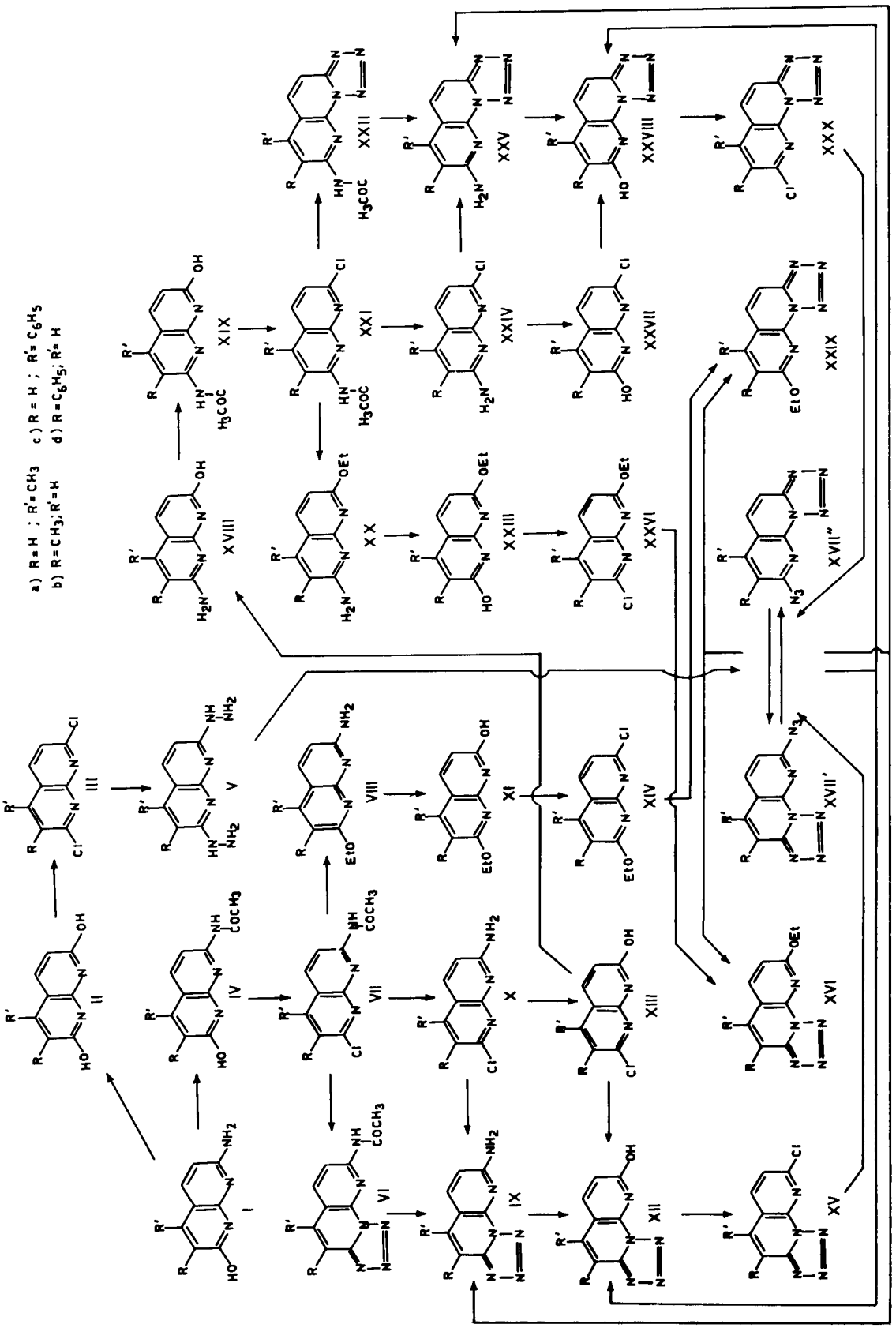


Chemical Shifts (δ)				Coupling constant, Hz
Ha	Hb	Hc	C_6H_5	Jab
7.83	8.70	8.66	7.65	8.4

Treatment of dichloronaphthyridine IIId with aqueous hydrazine produced the dihydrazino derivative Vd. Nitrosation of this dihydrazino derivative afforded a compound whose IR spectrum showed absorption indicative of the tetrazole nucleus in the region between 1110 and 1000 cm^{-1} and an intense band at 2140 cm^{-1} due to the presence of an azido group (see Figure 1). These observations suggest the nitrosation product to be one or the other, or possibly a mixture, of the azidotetrazole tautomers XVII′d and XVII″d. Differentiation on the basis of the synthetic routes employed is not possible since all of the synthetic procedures give the same solid material XVIId. This material was indeed prepared from acetylaminotetrazole VId after hydrolysis to IXd, treatment with nitrous acid to XIId, halogenation to XVd and reaction of XVd with sodium azide. The same compound XVIId was also obtained from 2-amino-7-hydroxy-3-phenyl-1,8-naphthyridine (XVIIId) (isomer of Id). This product was prepared by treatment of Xd with nitrous acid, followed by the reaction of the obtained XIIId with ammonia at 25-30 atm. The reaction sequence, which moves from naphthyridine XVIIId to compound XVIId, *via* XIXd, XXId, XXIId, XXVd, XXVIIId, and XXXd, is the same used for the conversion of Id to XVIId. The tetrazole derivatives IXd, XIId, XXVd and XXVIIId were also obtained from the chloro compounds Xd, XIIId, XXIVd and XXVIId, respectively by reaction with sodium azide.

In solution both tautomeric forms XVIId are present in a ring open-chain equilibrium XVII′d ⇌ XVII″d. Existence of an azidoazomethine-tetrazole equilibrium has been reported for several analogous heterocyclic systems (3a-d). In the present case the existence in solution of the equilibrium XVII′d ⇌ XVII″d is demonstrated by the observation that sodium ethoxide converts this material into a mixture of the two ethoxytetrazole derivatives XVId and XXIXd in the ratio of 10:1. Ethoxytetrazole XVId was also synthesized from acetylaminochloronaphthyridine XXId by treatment with sodium ethoxide to give XXd, followed by the reaction with nitrous acid. Compound XXIIId was converted to chloronaphthyridine XXVId, which gave XVId by treatment with sodium azide. The same procedure was followed to prepare ethoxytetrazole

SCHEME 1



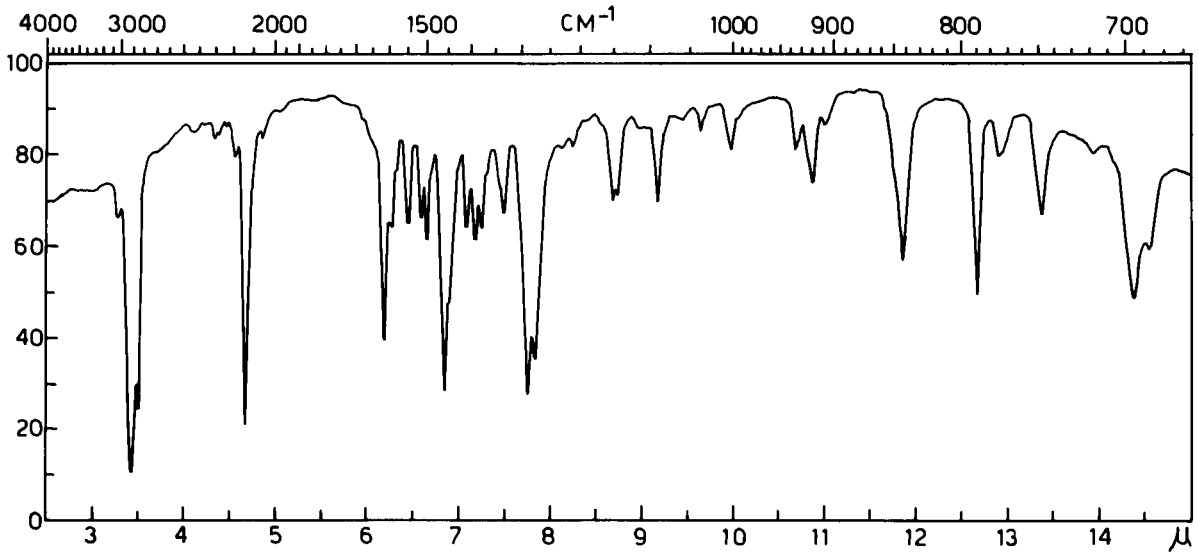


Figure 1. Infrared spectrum of XVIId in Nujol mulls.

derivative XXIXd (isomer of XVId), *via* VIIId, XId and XIVd. The proof of the structure of all tetrazole derivatives is based on elementary composition (see Experimental, Table I and Table II) and IR spectral data (see Table IV).

Catalytic reduction of XVIId reduces the azido group to the amino group and yields isomer IXd exclusively. Replacement of the azido group by a hydroxy group leads almost exclusively to isomer XIId.

These results suggest that the tetrazole nucleus is stabilized by conjugation when the phenyl group is present in an adjacent position; the stabilizing effect on the tetrazole nucleus by electron-donating groups is well known (3a-b). If in the present system the proximity of the phenyl group enhances the stability of one of the tautomeric forms, then we may speculate that the form that exists in the solid phase is XVII'd.

An analogous situation has previously been observed for the azidotetrazole XVIIb (4) where reactions involving the replacement of the azido group, gave mixtures of isomers IXb and XXVb, XIIb and XXVIIIb, XVIb and XXIXb and in each case the isomer having the tetrazole ring adjacent to the methyl group (IXb, XIIb and XVIb) was found to dominate.

Similarly, mixtures of isomers were formed from azidotetrazole XVIIc (5) by catalytic reduction (IXc and XXVc), by treatment with alcoholic potassium hydroxide (XIIc and XXVIIIc) and by treatment with sodium ethoxide (XVIc and XXIXc). However in these cases the more abundant isomer is the one in which the tetrazole nucleus is attached to the unsubstituted pyridine ring (XXVc, XXVIIIc and XXIXc). This dominance is very pronounced in the case of substitution by the amino group (IXc:XXVc - 1:10) and the ethoxy group (XVIc: XXIXc - 1:7), and less pronounced in the case of the hydroxy group (XIIc:XXVIIIc - 2:3). A similar situation was encountered for the azidotetrazole XVIIa (6).

The catalytic reduction of the hydroxytetrazolonaphthyridines XIId and XXVIIId was also examined. The starting materials were recovered unchanged from a basic medium (potassium hydroxide), while in an acidic medium (acetic acid) the naphthyridine Id was obtained from XXVIIId in 94% yield. From XIId, the naphthyridine XVIIId was obtained in 75% yield with about 14% of the starting material remaining unreduced. In our opinion, these observations indicate that, at least in the case of the hydroxytetrazole derivatives that have been examined, the phenyl group plays an important role, presumably due to its conjugation with the adjacent tetrazole ring in determining the preferential stability as in XIId (3a-b). However, of greater influence on the stabilization or destabilization of the tetrazolic structure in compounds XIId and XXVIIId is the *p*H of the medium. This is confirmed by the IR spectra of compounds XIId and XXVIIId where only the tetrazole form was observed in Nujol mulls or in dimethylformamide-pyridine solution (1:1); this is indicated by the absence of azido absorption bands in the 2200-2100 cm^{-1} region. In contrast to this, in trifluoroacetic acid solution, the azido group absorbs at 2140 cm^{-1}. Examination of the IR spectra of compounds VId, IXd, XVd, XXIId, XXVd, and XXXd under the same conditions leads to similar conclusions (7).

TABLE I

Chloro Derivatives Prepared	Hydroxy Derivatives Used	Reaction Time Minutes	Yield (a) %	M.p., °C	Molecular Formula	Analyses % Calcd. Cl	Calcd. N	Found Cl	Found N
IIId	IId	10	86.5	218-220 (b)	$C_{14}H_8Cl_2N_2$	25.77	10.18	25.50	10.13
XIVd	XId	10	87.3	156-158 (c)	$C_{16}H_{13}ClN_2O$	12.47	9.84	12.70	9.94
XVd	XIId	15	87.5	220-222 (dec.) (d)	$C_{14}H_8ClN_5$	12.61	24.92	13.00	24.85
XXId	XIXd	10	61.5	188-190 (e)	$C_{16}H_{12}ClN_3O$	11.91	14.12	12.16	13.90
XXVId	XXIIId	10	89.5	183-186 (c)	$C_{16}H_{13}ClN_2O$	12.47	9.84	12.73	9.77
XXXd	XXVIIId	20	53.0	255-257 (dec.) (d)	$C_{14}H_8ClN_5$	12.61	24.92	12.90	24.72

(a) Based on pure product isolated. (b) Sublimed at 195-200°/3-4 mm.. (c) Crystallized from glacial acetic acid-water. (d) Crystallized from glacial acetic acid. (e) Crystallized from ethanol-water.

TABLE II

Tetrazole Derivatives Prepared	Chloro Derivatives Used	Reaction Time Minutes	Yield (a) %	M.p., °C	Molecular Formula	Analyses % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IXd	Xd	60	35.0	300-303 (dec.) (b)	$C_{14}H_{10}N_6$	64.11	3.84	32.05	63.80	4.08	32.29
XIId	XIIId	120	54.5	249-251 (dec.) (b)	$C_{14}H_9N_5O$	63.87	3.45	26.61	63.97	3.22	26.85
XVId	XXVId	30	89.5	206-208 (b)	$C_{16}H_{13}N_5O$	65.97	4.50	24.04	65.70	4.44	23.87
XVIId	XVd or XXXd	30	32.5-34.4	204-206 (dec.) (b)	$C_{14}H_8N_8$	58.33	2.80	38.87	58.60	2.87	38.59
XXIId	XXId	30	91.2	230-233 (dec.) (c)	$C_{16}H_{12}N_6O$	63.15	3.98	27.62	63.00	3.80	27.96
XXVd	XXIVd	40	83.0	257-260 (dec.) (b)	$C_{14}H_{10}N_6$	64.11	3.84	32.05	63.91	4.08	31.96
XXVIIId	XXVIId	30	83.0	218-220 (dec.) (b)	$C_{14}H_9N_5O$	63.87	3.45	26.61	64.11	3.70	26.65
XXIXd	XIVd	10	88.0	185-188 (dec.) (b)	$C_{16}H_{13}N_5O$	65.97	4.50	24.04	65.96	4.80	24.09

(a) Based on pure compound isolated. (b) Crystallized from dimethylformamide-water. (c) Crystallized from glacial acetic acid-water.

TABLE III

Hydroxy Derivatives Prepared	Amino Derivatives Used	Reaction Time Minutes	Yield (a) %	M.p., °C	Molecular Formula	Analyses % Calcd. Cl	Calcd. N	Found Cl	Found N
IId	Id	15	95.0	293-295 (b)	$C_{14}H_{10}N_2O_2$	---	11.76	---	11.84
XId	VIIId	25	79.5	228-230 (c)	$C_{16}H_{14}N_2O_2$	---	10.52	---	10.53
XIIId	Xd	15	91.5	256-258 (d)	$C_{14}H_9ClN_2O$	13.82	10.91	14.13	10.88
XXIIId	XXd	25	96.0	180-182 (c)	$C_{16}H_{14}N_2O_2$	---	10.52	---	10.30
XXVIId	XXIVd	15	84.0	208-210 (e)	$C_{14}H_9ClN_2O$	13.82	10.91	13.45	11.16
XXVIIId (f)	XXVd	15	95.5						

(a) Based on pure compound isolated. (b) Sublimed at 260-270°/3-4 mm.. (c) Crystallized from glacial acetic acid-water. (d) Crystallized from ethanol. (e) Sublimed at 190-195°/2-3 mm.. (f) For Melting point, Molecular Formula and Analyses, see Table II.

TABLE IV

Compounds	Principal I.R. Peaks (cm^{-1}) in Nujol Mulls
Id	3450, 3200, 1620, 1600, 1515, 1375, 965, 885, 820, 703
IVd	3100, 1690, 1650, 1615, 1585, 1375, 1310, 820, 690
VId	3200, 1670, 1650, 1620, 1580, 1505, 1440, 1410, 1320, 1140, 1085, 900, 786, 687
IXd	3440, 3310, 3210, 1640, 1580, 1510, 1420, 1215, 1085, 1028, 782, 748, 690
XIId	1650, 1620, 1600, 1090, 1040, 848, 782, 690
XVd	1600, 1445, 1143, 1100, 1085, 787, 745, 693
XVId	1615, 1495, 1345, 1285, 1055, 833, 785, 690
XXIId	3110, 1685, 1630, 1585, 1490, 1410, 1295, 1240, 1085, 1000, 785, 700
XXVd	3490, 3300, 3180, 1635, 1580, 1510, 1440, 1090, 1000, 785, 705
XXVIIId	2550, 1625, 1590, 1530, 1425, 1350, 1220, 1120, 1085, 1050, 918, 828, 795, 705
XXIXd	1615, 1600, 1430, 1280, 1085, 1030, 788, 705
XXXd	1615, 1130, 1110, 1085, 930, 830, 782, 700

Similar behavior has been described for several analogous compounds (3a-b,8).

EXPERIMENTAL

All melting points were determined on a Kofler apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer in Nujol mulls. The proton NMR spectrum was obtained on a Jeol Model C 60 HL spectrometer in DMSO-d_6 at 100° with tetramethylsilane as internal reference. All the compounds are yellow or yellow-brown products except for the compounds IVd and XXId which are white.

7-Acetylamino-2-hydroxy-3-phenyl-1,8-naphthyridine (IVd).

A mixture of 5 g. of Id (1) (IR see Table IV) and 100 ml. of acetic anhydride was refluxed for 2 hours. After cooling, the precipitated solid was collected and washed with water. The product IVd was recrystallized from dimethylformamide to yield 4.2 g. (71.2%) of white crystals, m.p. above 310°; IR see Table IV.

Anal. Calcd. for $C_{16}H_{13}N_3O_2$: C, 68.80; H, 4.69. Found: C, 68.90; H, 4.44.

7-Acetylamino-2-chloro-3-phenyl-1,8-naphthyridine (VIId).

A mixture of 2 g. of IVd and 20 ml. of phosphorus oxychloride was refluxed for 45 minutes. After cooling, the solution was poured onto a mixture of ice and excess ammonium hydroxide. The precipitate which formed was collected by filtration and crystallized from ethanol, yield 1.6 g. (75.0%), m.p. 270-272°.

Anal. Calcd. for $C_{16}H_{12}ClN_3O$: N, 14.12; Cl, 11.92. Found: N, 13.91; Cl, 11.70.

Chloroderivatives IIId, XIVd, XVd, XXId, XXVId and XXXd were similarly prepared (see Table I).

8-Acetylamino-4-phenyltetrazolo[1,5-*a*][1,8]naphthyridine (VId).

To a suspension of 1 g. of VIId in 8 ml. of dimethylformamide was added 0.25 g. of sodium azide and the mixture was refluxed for 30 minutes. After cooling, the mixture was poured into water and the precipitate was collected, washed with water and dried. Crystallization from glacial acetic acid gave pure VId, yield 0.9 g.

(88.2%), m.p. 269-271° dec.

Anal. Calcd. for $C_{16}H_{12}N_6O$: C, 63.15; H, 3.98; N, 27.62. Found: C, 62.95; H, 3.78; N, 27.83.

Tetrazole derivatives IXd, XIId, XVId, XVIId, XXIId, XXVd, XXVIIId and XXIXd were similarly prepared (see Table II).

8-Amino-4-phenyltetrazolo[1,5-*a*][1,8]naphthyridine (IXd).

Compound IXd was also prepared in the following manner. A mixture of 1 g. of VId and 30 ml. of 10% aqueous sodium hydroxide was refluxed for 90 minutes. After cooling, the desired product IXd was collected and washed with water. Crystallization from dimethylformamide-water gave pure IXd, yield 0.78 g. (90.5%) (see Table II).

8-Amino-7-phenyltetrazolo[1,5-*a*][1,8]naphthyridine (XXVd).

By a procedure similar to that described for the preparation of IXd from VId, 2.8 g. of XXIId in 90 ml. of 10% aqueous sodium hydroxide gave 2.3 g. (95.0%) of practically pure XXVd (see Table II).

8-Hydroxy-4-phenyltetrazolo[1,5-*a*][1,8]naphthyridine (XIId).

To a cooled (0°) solution of 0.85 g. of IXd in 10 ml. of concentrated sulfuric acid was added 0.7 g. of sodium nitrite in small amounts. After standing at room temperature for 15 minutes the mixture was poured onto crushed ice and the solid (XIId) was collected. The product XIId was recrystallized from dimethylformamide-water, yield 0.67 g. (78.5%) (see Table II).

The hydroxy derivatives IId, XId, XIIId, XXIIId, XXVIId and XXVIIId were similarly prepared (see Table III).

7-Amino-2-ethoxy-3-phenyl-1,8-naphthyridine (VIIId).

To a solution of 20 ml. of absolute ethanol in which 0.3 g. of sodium metal had been dissolved, 1 g. of VIId was added. The reaction mixture was refluxed over a steam bath for 30 minutes, the solvent was removed by evaporation under reduced pressure; water was added and the product was collected and washed with water. Crystallization from cyclohexane gave pure VIIId, yield 0.75 g. (84.2%), m.p. 124-126°.

Anal. Calcd. for $C_{16}H_{15}N_3O$: N, 15.84. Found: N, 16.10.

2-Amino-7-ethoxy-3-phenyl-1,8-naphthyridine (XXd).

This compound was obtained from XXId and sodium ethoxide under conditions similar to those described for VIIId and crystallized from ethanol-water, yield 74.5%, m.p. 196-198°.

Anal. Calcd. for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.70; N, 15.84. Found: C, 72.28; H, 5.86; N, 15.45.

7-Amino-2-chloro-3-phenyl-1,8-naphthyridine (Xd).

A mixture of 1 g. of VIId in 10 ml. of 10% sulfuric acid was refluxed for 1 hour. After cooling, the mixture was made alkaline with concentrated ammonium hydroxide. The precipitate was collected and crystallized from ethanol-water to yield 0.73 g. (84.7%) of Xd, m.p. 237-239°.

Anal. Calcd. for $C_{14}H_{10}ClN_3$: Cl, 13.87; N, 16.43. Found: Cl, 13.95; N, 16.43.

2-Amino-7-chloro-3-phenyl-1,8-naphthyridine (XXIVd).

This compound was obtained from XXId and 10% sulfuric acid under conditions similar to those described for Xd and crystallized from ethanol, yield 88.0%, m.p. 265-267°.

Anal. Calcd. for $C_{14}H_{10}ClN_3$: Cl, 13.87; N, 16.43. Found: Cl, 14.17; N, 16.41.

2-Amino-7-hydroxy-3-phenyl-1,8-naphthyridine (XVIIId).

A mixture of 2.4 g. of XIIId and 60 ml. of absolute ethanol saturated with ammonia at 20-30° was heated in a stirred autoclave at 25-30 atm. for 48 hours at 150°. After cooling, the solid (XVIIId) was collected, washed with ethanol and then with water. Recrystallization from dimethylformamide gave 1.0 g. (45.0%) of pure XVIIId, m.p. 306-308°.

Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 71.07; H, 4.48; N, 17.40.

2-Acetylamino-7-hydroxy-3-phenyl-1,8-naphthyridine (XIXd).

A mixture of 9.7 g. of XVIIId and 150 ml. of acetic anhydride was refluxed for 2 hours and the resultant solution was evaporated to dryness *in vacuo*. The residue was suspended in concentrated ammonium hydroxide, collected and washed with water (9.8 g., 85.8%). This compound sublimed at 250-260°/2-3 mm. and melted at 280-282°.

Anal. Calcd. for $C_{16}H_{13}N_3O_2$: C, 68.80; H, 4.69. Found: C, 68.43; H, 4.69.

Synthesis of XVIId.

A mixture of 0.9 g. of IIId and 15 ml. of 85% aqueous hydrazine was refluxed for 8 hours. After standing overnight at room temperature, the solid was collected and dissolved in 250 ml. of 5% hydrochloric acid. The solution was then cooled to 0° and an excess of 5% aqueous solution of sodium nitrite was added dropwise with stirring. The mixture was kept at room temperature for 30 minutes and the precipitate was collected giving 0.75 g. (79.5%) of pure XVIId (see Table II).

Reaction of XVIId with Potassium Hydroxide.

A mixture of 0.63 g. of XVIId and 24 ml. of 5% ethanolic potassium hydroxide was refluxed for 1 hour. The resultant solution was evaporated to dryness *in vacuo* and the residual solid was dissolved in boiling water. Acidification of the hot filtered solution with concentrated sulfuric acid gave, after cooling, 0.54 g. (94.0%) of XIId.

Reaction of XVIId with Sodium Ethoxide.

To a solution containing 0.28 g. of sodium metal in 20 ml. of absolute ethanol was added 1.02 g. of XVIId; the mixture was heated under reflux for 1 hour. The solution was concentrated to give 0.8 g. (77.6%) of XVId. The ethanolic mother liquor for dilution with water gave 0.073 g. (7.1%) of XXIXd.

The Catalytic Reduction of XVIId.

A mixture of 0.5 g. of XVIId, 55 ml. of absolute ethanol and 5 ml. of 1 *N* acetic acid was hydrogenated in the presence of 0.2 g. of 10% palladium on charcoal catalyst at 3 atm. for 46 hours at room temperature. The mixture was extracted several times with boiling ethanol and the combined extracts were evaporated to dryness *in vacuo* to give 0.427 g. (94.0%) of IXd.

The reduction was repeated with the substitution of 12 ml. of 1.5 *N* ammonium hydroxide for 5 ml. of 1 *N* acetic acid to give a 97.0% yield of IXd.

The Catalytic Reduction of XXVIIId.

A mixture of 0.1 g. of XXVIIId in 30 ml. of absolute ethanol and 5 ml. of 1 *N* acetic acid was hydrogenated in the presence of 0.05 g. of 10% palladium on charcoal catalyst at 3 atm. for 46 hours at room temperature. The ethanolic solution, after separation from the catalyst, did not form a residue. The catalyst was extracted twice with 5 ml. of hot dimethylformamide and the solution and combined extracts were concentrated to one ml. This solution diluted with water gave 0.085 g. (94.1%) of Id.

The reduction was repeated with substitution of 5 ml. of 1 *N*

potassium hydroxide for 5 ml. of 1 *N* acetic acid. The catalyst was collected, washed with ethanol and the combined ethanolic solution was evaporated to dryness. The residue was treated with 10% hydrochloric acid and the insoluble solid was filtered to give 0.096 g. (96.0%) of unreacted product.

The Catalytic Reduction of XIId.

The compound XIId (0.1 g.) was hydrogenated in acetic acid by the same procedure described above for XXVIIId. The ethanolic solution, after filtration gave 0.033 g. of a mixture of XIId and XVIIId (1:2). The catalyst was extracted twice with 5 ml. of hot dimethylformamide and after concentrating to 2 ml., 0.044 g. (48.7% yield) of XVIIId separated from the combined extracts. The mother liquor diluted with water gave 0.005 g. of a mixture of XIId and XVIIId (1:1).

The reduction was repeated with the substitution of 5 ml. of 1 *N* potassium hydroxide for 5 ml. of 1 *N* acetic acid. Using a procedure similar to that for XXVIIId, 93% of starting material was recovered.

Oxidation of 8-Acetylamino-4-phenyltetrazolo[1,5-*a*][1,8]naphthyridine (VId).

To a solution of 1 g. of VId in 15 ml. of hot glacial acetic acid was added 500 ml. of boiling water. This solution, heated on steam bath with stirring, was treated dropwise with an excess of 5% aqueous potassium permanganate. The heating was continued for 1 hour and excess potassium permanganate was destroyed with ethanol; the filtered solution was concentrated at reduced pressure to 40 ml., acidified with nitric acid, boiled for 30 minutes and, after cooling, treated with an excess of 10% aqueous silver nitrate. The resulting precipitate was collected, heated on a steam bath in 10 ml. of 10% hydrochloric acid for 15 minutes and the mixture was filtered; the filtrate was evaporated to dryness under reduced pressure. The residue, kept one day in an evacuated desiccator over soda lime and calcium chloride, was dissolved in hot ethyl acetate. The solution was filtered and the solvent removed *in vacuo*. The residual product, suspended in petroleum ether (b.p. 60-80°), gave 0.3 g. of solid, which was treated with hot benzene leaving 0.03 g. of undissolved tetrazole, m.p. 156-157°.

The benzene solution, after concentrating, gave 0.16 g. of 5-benzoyltetrazole, m.p. 139-141°. This solid was identical (m.p., infrared spectra) with an authentic sample.

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(7) The IR spectra of XVId and XXIXd shows a small azido absorption band at 2140 cm^{-1} also in Nujol mulls and dimethylformamide-pyridine (1:1) solution.

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