Azinotriazines. I. Synthesis and Spectral Data of Pyrido[3,2-*e*]-*as*-triazines

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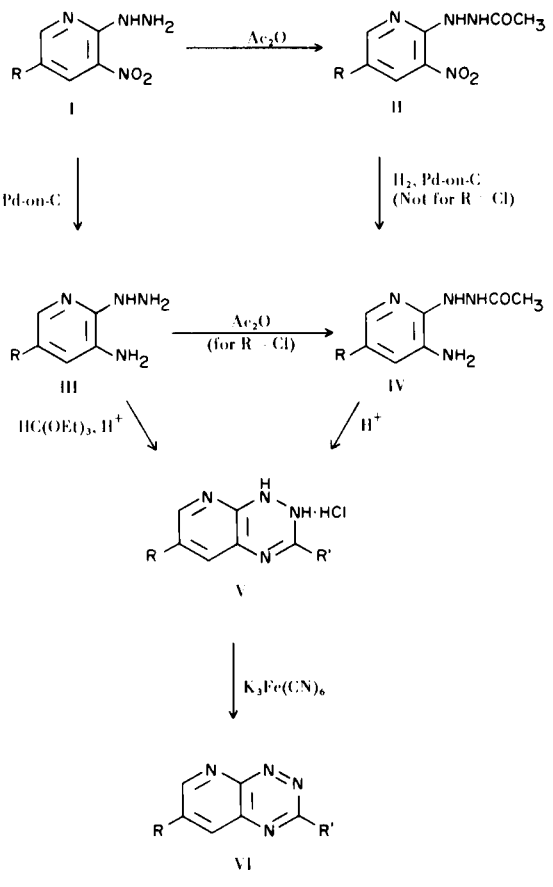
A series of pyrido[3,2-*e*]-*as*-triazines (VI) was prepared *via* acid-catalyzed cyclization of suitable 2-substituted 3-aminopyridines obtained by reduction of the corresponding 3-nitropyridines. Cyclization of 3-amino-2-hydrazinopyridines (III) with triethyl orthoformate and hydrochloric acid, or cyclodehydration of 2-(2-acetylhydrazino)-3-aminopyridines (IV) with alcoholic hydrogen chloride gave 1,2-dihydropyrido[3,2-*e*]-*as*-triazine hydrochloride (V). Mild dehydrogenation with alkaline potassium ferricyanide yielded heteroaromatic pyrido[3,2-*e*]-*as*-triazines (VI), for which ultraviolet and nmr spectral data are reported.

There are eight possible pyridotriazines, if those with bridgehead nitrogen atoms are excluded. Examples of only two of these eight bicyclic heteroaromatic systems are known: derivatives of pyrido[2,3-*e*]-*as*-triazine prepared by base-catalyzed cyclization of 2-guanidino-3-nitropyridines (1) and a pyrido[3,2-*d*]-*v*-triazine prepared by diazotization of 3-aminopyridine-2-hydroxamic acid (2).

SCHEME I



Series a: R = H
Series b: R = Cl
Series c: R = CO_2CH_3

An interest in the chemistry of azinoazines (3) led us to prepares derivatives of some of the other pyridotriazine ring systems. The synthesis of a series of pyrido[3,2-*e*]-*as*-triazines, including the parent compound, is described in this paper. Syntheses of derivatives of the two remaining pyrido-*as*-triazine systems are described in the following paper.

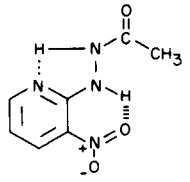
The pyrido[3,2-*e*]-*as*-triazine ring system was formed by cyclization of suitably substituted pyridines. Both intramolecular cyclodehydration of 3-amino-2-(2-acylhydrazino)pyridines (IV), an extension of the Bischler synthesis of benzo-*as*-triazines (4,5), and intermolecular cyclization of 3-amino-2-hydrazinopyridines (III) with a one-carbon unit were used to give 1,2-dihydropyrido-[3,2-*e*]-*as*-triazines (V) as shown in Scheme I.

2-Hydrazino-3-nitropyridines (I) were prepared by treatment of appropriate 2-halo-3-nitropyridines with ethanolic hydrazine hydrate (1-2 hours, 25°). The desired amine (IIIa) was not obtained in one step from 3-amino (or 3-acetamido)-2-chloropyridine and hydrazine (or methylhydrazine) under more vigorous conditions (100°, 5 hours); 70-90% of starting materials was recovered. Selective reduction of the nitro group in Ia without concurrent cleavage of the N–N bond in the desired hydrazinopyridine could not be obtained with Raney nickel. However, when palladium-on-carbon was used as catalyst, the nitropyridines I were reduced rapidly to 2-amino-3-hydrazinopyridines (III) in good yield. These compounds were not kept for prolonged periods as they are sensitive to air oxidation. The treatment of a suspension of III in triethyl orthoformate with hydrochloric acid (6) at room temperature gave 1,2-dihydropyrido[3,2-*e*]-

as-triazine hydrochlorides (V, R′=H).

2-(2-Acetylhydrazino)-3-nitropyridines (II) were prepared from I with acetic anhydride at room temperature. These compounds gave deep purple solutions in alkali, presumably due to formation of tautomeric *aci*-nitroforms.

2-(2-Acetylhydrazino)-3-nitropyridine (IIa) exists as two interconvertible polymorphs: red plates (from benzene) which change to orange at 120° without melting. The color change is not reversed on cooling, and the red form is obtained again on recrystallization. As required for polymorphs, the infrared and ultraviolet spectra of both forms in solution are identical while the infrared spectra taken in potassium bromide disks are quite different. The red form shows strong intermolecular hydrogen-bonding expected of an acylhydrazine in the solid state (7) (3240 cm^{-1}, bonded NH stretching; 1630 cm^{-1}, bonded C=O stretching). The orange form gives a spectrum similar to that obtained in solution (1700 cm^{-1}, non-bonded C=O stretching) but with bonded rather than non-bonded NH stretching (at 3260 cm^{-1}).



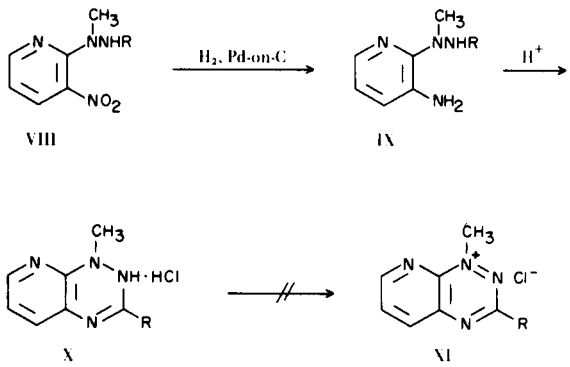
VII

This suggests that in the orange form there is intramolecular bonding of the two hydrogens on the acylhydrazine nitrogen atoms to the nitro group and the pyridine nitrogen, as in VII, leaving no hydrogen atom capable of forming an intermolecular hydrogen-bond to the carbonyl oxygen atom as in the red form. Similar intramolecular hydrogen-bonding in *o*-nitroacetanilides has been extensively studied (8).

In series a and c, reduction of the nitro group in II using palladium-on-carbon as catalyst occurred rapidly to give the amine IV. In series b however, no amine was obtained presumably due to partial hydrogenolysis of the 5-chloro substituent and subsequent cyclization of the resulting mixture of acetylhydrazinoaminopyridines catalyzed by the hydrogen chloride generated. The amine IVb was prepared by selective acetylation of IIIb with one equivalent of acetic anhydride in ether at room temperature. Cyclodehydration of the amines IV occurred rapidly at room temperature with 6 *N* alcoholic hydrogen chloride to give 1,2-dihydropyrido[3,2-*e*]-*as*-triazine hydrochlorides (V, R′=CH_3).

Although benzimidazoles are by-products of the Bischler synthesis of benzo-*as*-triazines (5,9), no imidazo-[4,5-*b*]pyridine formation was observed with the mild cyclization conditions used here. Benzimidazoles result from cyclization of *o*-acylaminophenylhydrazines formed either by acyl-group migration from *o*-acylhydrazinoanilines (5,9) or by ring opening of the initially formed dihydrobenzo-*as*-triazines. Under suitable conditions, such as heating with anhydrous organic acids, *o*-acylhydrazinoanilines can be cyclized to benzimidazoles in good yield (10).

SCHEME II



Mild treatment of the hydrochlorides Va (R′=H or CH_3) with base gave dihydropyridotriazines as yellow solids, sensitive to air oxidation. Brief treatment of the hydrochlorides V with alkaline potassium ferricyanide gave good yields of the aromatic pyrido[3,2-*e*]-*as*-triazines (VI). The methyl esters VIc (R′=H or CH_3) were hydrolyzed under mild alkaline conditions to the corresponding carboxylic acids.

1-Methyl-1,2-dihydropyridotriazines (X, R=H or CH_3) were prepared by the same reaction sequence using methylhydrazine instead of hydrazine (Scheme II). Attempts to convert X to 1-methylpyridotriazinium chlorides (XI) using oxygen with ferric chloride or platinum (11) resulted in recovery of starting material only.

The pyrido[3,2-*e*]-*as*-triazines (VI) were orange or red crystalline solids, and the parent heterocycle VIa (R=R′=H) was appreciably soluble in water (about 25 mg./ml. at 25°). The ultraviolet spectra (Table I) exhibit three main bands, which from their position and intensity are assumed to be $\pi \rightarrow \pi^*$ bands, and a longer wavelength absorption identified as a $n \rightarrow \pi^*$ band by its low intensity and its shift to longer wavelength in non-polar solvents. The 3-methyl, 6-chloro and 6-carbomethoxy substituents all cause a bathochromic shift of the first $\pi \rightarrow \pi^*$ band.

The nmr spectrum of the parent heterocycle VIa (R′=H) exhibits a sharp singlet at very low field (τ -0.11) which is assigned to H_3 as this proton is subject to the *N*-anisotropy of two adjacent nitrogen atoms (12). This assignment is confirmed by the absence of this peak in the nmr spectrum of the 3-methyl derivative VIa (R′=CH_3). The assignment for the pyrido ring protons follows from a

TABLE I

Electronic Absorption Spectra (a) of Pyrido[3,2-*e*]-*as*-triazines

Compound	λ max mμ (ε)				
VIa, R′=H	<210 (>28,000)	283 (Sh) (3700)	305 (6530)	315 (5680)	475 (200)
VIb, R′=H	<210 (>23,900)	282 (Sh) (3330)	312 (8320)	325 (8160)	470 (230)
VIc, R′=H	<210 (>24,800)	262 (4750)	314 (5320)	325 (4750)	475 (195)
VI, R=CO_2H, R′=H	<210 (>21,000)	268 (3610)	312 (6160)	322 (5540)	475 (180)
VIa, R′=CH_3	<210 (>22,700)	270 (4380)	312 (6720)	325 (6020)	480 (230)
VIb, R′=CH_3	<210 (>30,300)	282 (Sh) (3430)	315 (8840)	330 (9384)	475 (280)
VIc, R′=CH_3	<210 (>36,100)	268 (4385)	320 (7140)	332 (6530)	495 (210)
VI, R=CO_2H, R′=CH_3	<210 (>28,900)	268 (3700)	320 (6930)	332 (6270)	490 (175)

(a) In ethanol solution.

TABLE II

Proton Chemical Shifts (τ) and Coupling Constants (cps) for Pyrido[3,2-*e*]-*as*-triazines (In Deuteriochloroform Solution)

Compound	τ 3	τ 5	τ 5	τ 7	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$
VIa, R′=H	-0.11	1.43	1.88	0.60	8.6	2.0	3.8
VIb, R′=H	-0.07	1.48	---	0.77	---	2.6	---
VIc, R′=H	-0.18	0.90	5.87 (a)	0.22	---	2.2	---
VI, R=CO_2H, R′=H (b)	-0.35	1.00	---	0.32	---	2.2	---
VIa, R′=CH_3	6.80 (c)	1.62	2.02	0.74	8.6	1.8	4.0
VIb, R′=CH_3	6.80 (c)	1.65	---	0.90	---	2.5	---
VIc, R′=CH_3	6.77 (c)	1.07	5.92 (a)	0.35	---	2.1	---
VI, R=CO_2H, R′=CH_3 (b)	6.83 (c)	1.18	---	0.43	---	2.1	---

(a) Carbomethoxy protons. (b) In d_6-dimethylsulfoxide solution. (c) Methyl protons.

comparison with the chemical shifts and coupling constants for substituted pyridines (13) and the assignment of the high-field quartet to H_6 is confirmed by the absence of this peak in the nmr spectrum of the 6-chloro derivative VIb (R′=H). The complete assignments of the relative chemical shifts and coupling constants for the pyrido-[3,2-c]-*as*-triazines are given in Table II.

EXPERIMENTAL (14)

2-Hydrazino-3-nitropyridine (Ia).

Hydrazine hydrate (20 g., 0.4 mole) was added dropwise to a stirred, partial solution of 2-chloro-3-nitropyridine (31.7 g., 0.2 mole) in ethanol (200 ml.). After the addition was complete, the reaction mixture was stirred for 3 hours and then concentrated under reduced pressure. Water (250 ml.) was added to the residue and the mixture extracted with chloroform (five 100 ml. portions). The combined extracts were dried (magnesium sulfate), filtered and the chloroform removed under reduced pressure to yield the crude hydrazinopyridine Ia.

In the same manner, 2-bromo-5-chloro-3-nitropyridine (15), reaction time 2 hours, gave Ib; 5-carbomethoxy-2-chloro-3-nitropyridine (16), reaction time 15 minutes, gave Ic and 2-chloro-3-nitropyridine with methylhydrazine, reaction time 3 hours, gave VIII (R=H). The respective crystallizing solvents, melting points, etc., are given in Table III.

2-(2-Acetylhydrazino)-3-nitropyridine (IIa).

2-Hydrazino-3-nitropyridine (10.8 g., 0.07 mole) was stirred with acetic anhydride (50 ml., 0.53 mole) for 1 hour. The reaction mixture was poured into water (500 ml.), neutralized with sodium hydroxide solution and extracted with chloroform (five 100 ml. portions). The combined extracts were dried (magnesium sulfate), filtered and the chloroform removed under reduced pressure to yield the crude product IIa.

In exactly the same manner Ib, Ic and VIII (R=H) were converted to IIb, IIc and VIII (R=$COCH_3$), respectively. The crude products were recrystallized as described in Table III.

3-Amino-2-hydrazinopyridine (IIIa).

A partial solution of 2-hydrazino-3-nitropyridine (7.7 g., 0.05 mole) in ethanol (100 ml.) containing 0.5 g. of 10% palladium-on-carbon was hydrogenated at 35 psi in a Parr hydrogenator. Uptake

TABLE III

Compound	M.p., °C	Yield %	Form	Recryst. Solvent (a)	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
2-Hydrazino-3-nitropyridines											
Ia	171-172	81	orange needles	E	$C_5H_6N_4O_2$	39.0	3.9	36.4	39.0	4.2	36.6
Ib	134-135	91	red needles	B	$C_5H_5ClN_4O_2$ (b)	31.8	2.7	29.8	32.0	2.7	29.8
Ic	169-170	60	orange needles	B	$C_7H_8N_4O_4$	39.6	3.8	26.4	39.7	3.8	26.6
VIII, R=H	60-61	84	orange prisms	E	$C_6H_8N_4O_2$	42.9	4.8	33.3	42.7	4.8	33.1
2-(2-Acetylhydrazino)-3-nitropyridines											
IIa	157-158	65	red plates (c)	B	$C_7H_8N_4O_3$	42.9	4.1	28.6	43.0	4.3	29.0
IIb	171-172	83	yellow needles	B	$C_7H_7ClN_4O_3$ (d)	36.5	3.1	24.3	36.2	3.2	24.1
IIc	201-202	67	yellow needles	C	$C_9H_{10}N_4O_5$	42.5	4.0	22.0	42.1	3.8	21.9
VIII, R=$COCH_3$	155-156	70	yellow prisms	B	$C_8H_{10}N_4O_3$	45.7	4.8	26.7	45.9	4.8	26.4
3-Amino-2-hydrazinopyridines											
IIIa	111-112	81	white plates	B	$C_5H_8N_4$	48.4	6.5	45.1	48.7	6.4	44.8
IIIb	168-169	64	white needles	B	$C_5H_7ClN_4$ (e)	37.9	4.5	35.3	38.1	4.5	35.2
IIIc	208-209	63	ivory needles	M	$C_7H_{10}N_4O_2$	46.2	5.5	30.8	46.0	5.3	30.6
IX, R=H	106-107	72	white plates	B	$C_6H_{10}N_4$	52.2	7.3	40.6	52.1	7.3	41.0
2-(2-Acetylhydrazino)-3-aminopyridines											
IVa	153-155	61	ivory needles	C	$C_7H_{10}N_4O$	50.6	6.1	33.7	50.3	6.1	33.6
IVb	154-155	71	ivory needles	C	$C_7H_9ClN_4O$ (f)	41.9	4.5	27.9	42.3	4.6	27.9
IVc	198-200	68	white prisms	M	$C_9H_{12}N_4O_3$	48.2	5.4	25.0	48.5	5.4	24.5
IX, R=$COCH_3$	128-129	70	ivory needles	B	$C_8H_{12}N_4O$	53.3	6.7	31.1	53.3	6.6	31.2

(a) B = benzene, C = chloroform, E = ethanol, M = methanol. (b) Cl, Calcd: 18.8; Found: 19.2. (c) Polymorphic. (d) Cl, Calcd.: 15.4; Found: 15.8. (e) Cl, Calcd: 22.4; Found: 22.6. (f) Cl, Calcd: 17.7; Found: 18.0.

TABLE IV

Compound	M.p., °C	Yield %	Form	Recryst. Solvent (a)	Formula	Calcd., % C	H	N	Cl	Found, % C	H	N	Cl
1,2-Dihydropyrido[3,2-*e*]-*as*-triazine Hydrochlorides (b)													
Va, R′=H	182-184	81	yellow	E	$C_6H_7ClN_4$	42.3	4.1	32.9	20.8	42.3	4.2	33.0	20.9
Vb, R′=H	218 (c)	87	yellow	E	$C_6H_6Cl_2N_4$	35.1	2.9	27.3	34.6	35.4	3.1	27.1	34.1
Vc, R′=H	192-193	80	orange	M	$C_8H_9ClN_4O_2$	42.0	4.0	24.5	15.4	41.8	4.4	23.7	15.5
Va, R′=CH_3	220	60	yellow	E	$C_7H_{10}Cl_2N_4$ (d)	38.1	4.6	25.3	32.1	38.2	4.8	25.5	32.6
Vb, R′=CH_3	240 (c)	77	yellow	E	$C_7H_8Cl_2N_4$	38.4	3.7	25.6	32.4	38.5	3.6	25.7	32.0
Vc, R′=CH_3	237-239	83	orange	M	$C_9H_{11}ClN_4O_2$	44.5	4.6	23.1	14.6	44.2	4.7	23.2	14.7
X, R=H	245 (c)	63	yellow	E	$C_7H_9ClN_4$ (e)	43.4	5.2	28.9	18.3	43.7	5.1	28.8	18.7
X, R=CH_3	270 (c)	86	yellow	E	$C_8H_{11}ClN_4$	48.4	5.6	28.2	17.8	48.2	5.7	28.0	17.7
Pyrido[3,2-*e*]-*as*-triazines													
VIa, R′=H	151-152	86	orange plates	B	$C_6H_4N_4$	54.5	3.1	42.4		54.7	3.0	42.4	
VIb, R′=H	125-126	87	orange prisms	B	$C_6H_3ClN_4$	43.3	1.8	33.6	21.3	43.0	1.8	34.0	21.6
VIc, R′=H	131-132	77	red plates	B	$C_8H_6N_4O_2$	50.5	3.2	29.5		50.7	3.5	29.9	
VI, R=CO_2H, R′=H	235 dec	55	red plates	A	$C_7H_4N_4O_2$	47.7	2.3	31.8		47.7	2.8	32.1	
VIa, R′=CH_3	171-172	82	orange needles	B	$C_7H_6N_4$	57.5	4.1	38.3		57.4	4.2	38.3	
VIb, R′=CH_3	129-130	82	orange prisms	B	$C_7H_5ClN_4$	46.6	2.8	31.0	19.6	46.5	3.1	31.0	19.8
VIc, R′=CH_3	217-218	71	red needles	B	$C_9H_8N_4O_2$	52.9	4.0	27.4		53.3	4.0	27.3	
VI, R=CO_2H, R′=CH_3	215 dec	60	red plates	A	$C_8H_6N_4O_2$	50.5	3.2	29.5		50.4	3.3	29.8	

(a) A = ethyl acetate, B = benzene, E = ethanol, M = methanol. (b) The hydrochlorides were amphorous solids which decomposed on melting. (c) Sample darkened about 20° below m.p. (d) Dihydrochloride. (e) Hemihydrate, calculated for 0.5 H_2O; Karl Fischer, Calcd: 4.7; Found: 5.8.

of hydrogen was complete in 30 minutes. The catalyst was removed by filtration, and the filtrate evaporated to dryness under reduced pressure to give the crude aminopyridine IIIa.

In the same way, the aminopyridines IIIb, IIIc, IVa, IVc, IX (R=H) and IX (R=$COCH_3$) were prepared by hydrogenation of Ib, Ic, IIa, IIc, VIII (R=H) and VIII (R=$COCH_3$), respectively. The crystallizing solvent, melting points, etc., for three of these compounds are given in Table III.

2-(2-Acetylhydrazino)-3-amino-5-chloropyridine (IVb).

Acetic anhydride (8.2 g., 0.08 mole) was added dropwise to a stirred partial solution of 3-amino-5-chloro-2-hydrazinopyridine (12.7 g., 0.08 mole) in ether (300 ml.). Stirring was continued for 1 hour after addition was complete. The product was isolated by filtration and recrystallized from chloroform (see Table III).

1,2-Dihydropyrido[3,2-*e*]-*as*-triazine Hydrochloride (Va, R'=H).

To a stirred suspension of 3-amino-2-hydrazinopyridine (2.48 g., 0.02 mole) in triethyl orthoformate (25 ml.) was added concentrated hydrochloric acid (3.5 ml., 0.04 mole). Stirring was continued for 2 hours, then the product was isolated by filtration and washed with ether.

The hydrochlorides Vb (R'=H), Vc (R'=H) and X (R=H) were prepared in the same manner from IIIb, IIIc and IX (R=H), respectively. The crystallizing solvents, melting points, etc., for these compounds are given in Table IV.

1,2-Dihydro-3-methylpyrido[3,2-*e*]-*as*-triazine Dihydrochloride (Va, R'=CH_3).

To a solution of 2-(2-acetylhydrazino)-3-aminopyridine (3.3 g., 0.02 mole) in ethanol (30 ml.) was added 6 *N* ethanolic hydrogen chloride (30 ml.). The solution immediately became bright yellow, and it was evaporated to dryness under reduced pressure to give the crude product.

In similar manner, IVb, IVc and IX (R=$COCH_3$) were cyclized to give the hydrochlorides Vb (R'=CH_3), Vc (R'=CH_3) and X (R=CH_3). Crystallizing solvents, melting points, etc., are given in Table IV.

1,2-Dihydropyrido[3,2-*e*]-*as*-triazine.

A solution of the hydrochloride Va (R'=H) (1.7 g., 0.01 mole) in water (20 ml.) was made basic with ammonium hydroxide and immediately extracted with chloroform (five 20 ml. portions). The combined extracts were dried (magnesium sulfate), filtered and the chloroform removed under reduced pressure. The residue was recrystallized from benzene to give 0.49 g. (36%) of the dihydropyridotriazine as bright yellow prisms, m.p. 135° dec.; ir (potassium bromide) 3300 cm^{-1} (NH).

Anal. Calcd. for $C_6H_6N_4$: C, 53.7; H, 4.5; N, 41.8. Found: C, 53.9; H, 4.5; N, 41.9.

1,2-Dihydro-3-methylpyrido[3,2-*e*]-*as*-triazine.

A suspension of dihydrochloride Va (R'=CH_3) (2.21 g., 0.01 mole) and sodium carbonate (5.0 g., 0.06 mole) in acetone (200 ml.) was stirred under an atmosphere of nitrogen for 3 hours. The solution was filtered and evaporated under reduced pressure. The residue was recrystallized from benzene to give 0.58 g. (43%) of the dihydropyridotriazine as yellow prisms, m.p. 158° dec.; ir (potassium bromide) 3300 cm^{-1} (NH).

Anal. Calcd. for $C_7H_8N_4$: C, 56.7; H, 5.4; N, 37.8. Found: C, 56.4; H, 5.5; N, 38.2.

Pyrido[3,2-*e*]-*as*- triazine (VIa, R'=H).

A solution of the hydrochloride (Va, R=H) (3.41 g., 0.02 mole) in water (50 ml.) was made basic with ammonium hydroxide and a solution of potassium ferricyanide (6.58 g., 0.02 mole) in water (50 ml.) was added with stirring. The mixture was extracted with chloroform (five 100 ml. portions). The combined extracts were dried (magnesium sulfate), filtered and the chloroform removed under reduced pressure to give the crude pyridotriazine VIa (R=H).

In the same manner, the hydrochlorides Va (R'=CH_3, Vb (R'=H and CH_3) and Vc (R'=H and CH_3) were converted to the pyridotriazines VIa (R'=CH_3), VIb (R'=H and CH_3) and VIc (R'=H and CH_3), respectively. Recrystallization solvents, melting points, etc., are given in Table IV.

Hydrolysis of 6-Carbomethoxypyrido[3,2-*e*]-*as*-triazines (VIc, R=H and CH_3).

The above methyl esters (2 mmoles) in methanol (2 ml.) were stirred with a solution of potassium hydroxide (2.2 mmoles) in water (2 ml.) for 16 hours. The reaction mixture was diluted with water (10 ml.), washed with chloroform (three 10 ml. portions) and, after careful acidification to *p*H 1, extracted with ethyl acetate (three 15 ml. portions). The combined extracts were washed with water (15 ml.), dried (magnesium sulfate), filtered and the ethyl acetate removed under reduced pressure. The products VI (R=CO_2H, R'=H) and VI (R=CO_2H, R'=CH_3) are described in Table IV.

Acknowledgments.

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