S. W. Schneller and D. G. Bartholomew*

Department of Chemistry, University of South Florida, Tampa, Florida 33620

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Cyclization of *N*-acyl-*N'*-(6-chloropyrid-2-yl)hydrazines (**2a-2e**) with phosphorus oxychloride has produced several 5-chloro-*s*-triazolo[4,3-*a*]pyridines (**3a-3e**). Nucleophilic displacement of the chlorosubstituent of 5-chloro-*s*-triazolo[4,3-*a*]pyridine (**3a**) availed the 5-ethoxy (**4a**) and 5-thioethoxy (**4b**) derivatives and di(*s*-triazolo[4,3-*a*]pyrid-5-yl)sulfide (**8**) while reaction of 5-ethylsulfonyl-*s*-triazolo[4,3-*a*]pyridine (**4d**) with potassium hydroxide yielded the 5-hydroxy/5-one system (**4c** or **6**). Further reaction of **3a** with bromine to give 3-bromo-5-chloro-*s*-triazolo-[4,3-*a*]pyridine (**3g**) has provided the corresponding 3-cyano- and 3-carboxamido-5-chloro-*s*-triazolo[4,3-*a*]pyridine derivatives (**3h** and **3i**). Treatment of 6-chloro-2-hydrazinopyridine (**1**) with cyanogen bromide has provided 3-amino-5-chloro-*s*-triazolo[4,3-*a*]pyridine (**3f**) which, with bromoacetaldehyde dimethyl acetal, transformed into 7-chloroimidazo[1,2-*b*]-*s*-triazolo[4,3-*a*]-pyridine (**7**). Finally, attempts at cyclizing *N*-oxalyl-*N'*-(6-chloropyrid-2-yl)hydrazine derivatives (**2g-2i**) with intentions of preparing various 3-acyl-5-chloro-*s*-triazolo[4,3-*a*]pyridines for entry into other 3,5-disubstituted systems were unsuccessful.

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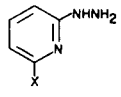
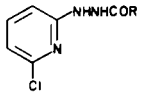
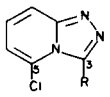
To date little attention (1) has been devoted to the synthesis of 5-substituted- and 3,5-disubstituted-*s*-triazolo-[4,3-*a*]pyridines. We have found, however, that a potentially fruitful route to such derivatives can be accomplished from 6-chloro-2-hydrazinopyridine (**1**). Therefore, reaction of **1** with an appropriate carboxylic acid or its acid chloride (1a,2) yielded the acylated derivatives **2a-2e** which, upon treatment with phosphorus oxychloride (1a), availed the 5-chloro-*s*-triazolo[4,3-*a*]pyridine series **3a-3e**.



1, X = Cl
5, X = OH

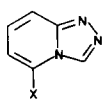


2
a, R = H
b, R = Me
c, R = Et
d, R = *t*-Bu
e, R = CH_2Cl
f, R = OEt
g, R = $CONH_2$
h, R = CO_2Me
i, R = CO_2Et

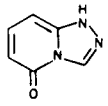


3
a, R = H
b, R = Me
c, R = Et
d, R = *t*-Bu
e, R = CH_2Cl
f, R = NH_2
g, R = Br
h, R = CN
i, R = $CONH_2$
j, R = CO_2R' (R' = Me, Et)

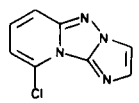
Reaction of **3a** with sodium ethoxide and potassium thioethoxide led to **4a** and **4b**, respectively, but treatment of **3a** with sodium hydroxide in an attempt to prepare the 5-hydroxy derivative (**4c**) yielded a complex mixture of products. Plans at synthesizing **4c** from **5**, following the above scheme to **3**, were abandoned when numerous attempts to prepare **5** from 2-chloropyridin-6-ol failed.



4
a, X = OEt
b, X = SEt
c, X = OH
d, X = SO_2Et
e, X = NH_2
f, X = SH



6



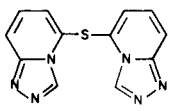
7

Compound **4c**, however, was successfully synthesized upon oxidizing **4b** with *m*-chloroperoxybenzoic acid to the sulfone **4d** and subjecting **4d** to reaction with 9% potassium hydroxide. Inspection of the infrared and pmr spectra (Table II) for **4c** suggests that it exists predominantly in the keto tautomer **6**.

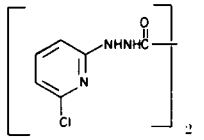
Unfortunately, the adenine-like analog **4e** could not be prepared from either **3a** or **4d** and ammonia, leading to recovery of unreacted **3a** in the former case and an intractable mixture of products in the latter. However, the 3-amino compound (**3f**) was available from **1** and cyanogen bromide and reaction of **3f** with bromoacetaldehyde diethyl acetal produced the tricyclic ring system **7**.

In view of the biological properties of 6-mercaptopurine (3) reaction of **3a** with thiourea with the intention of availing **4f** produced **8** as the only product. Compound **8** apparently arose from initial formation of **4f** whose nucleophilic mercapto functionality was sufficiently reactive to displace the 5-chlorosubstituent of a second molecule of **3a**. Attempts to alter this result were unsuccessful.

Bromination of **3a** formed **3g** which, in turn, could be converted to **3h** with cuprous cyanide. The structure of **3h** was supported by its spectral data (see Experimental) and hydration to **3i** even though successful microanalytical data for a chromatographically pure sample of **3h** could not be achieved. In an alternative approach to **3h**, **1** was treated with ethyl cyanoformate in hopes of obtaining **2**



8



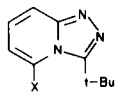
9

(R = CN) which could be cyclized with phosphorus oxychloride (as in the preparation of **3a-3e**). However, the cyano group of ethyl cyanoformate was displaced by the therminal amino portion of **1** yielding **2f**. This result is not

surprising in view of Dornow and Grabhöfer's report (4) that ethyl cyanoformate is a good carboethoxylation agent.

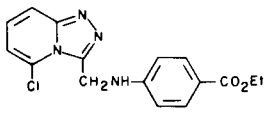
Reaction of **1** with ethyl oxamate formed **2g**; however, numerous attempts at its cyclo-dehydration to **3i** led to complete recovery of starting material. Finally treatment of **1** with dimethyl oxalate yielded **2h** and **9** while **1** with diethyl oxalate produced only **2i**. As with **2g**, **2h** and **2i** could not be induced to cyclize to **3j** which would have been a useful synthetic intermediate for entry into a variety of 3,5-disubstituted-*s*-triazolo[4,3-*a*]pyridines.

In an effort to disclose the steric restrictions to nucleophilic attack at C-5 of **3d**, **3d** was reacted with potassium thioethoxide and found to produce **10a**. Attempts to oxidize **10a** to **10b** failed as did reaction of **10a** with sodium



10

a, X = SEt
b, X = SO_2Et
c, X = OH



11

hydroxide in hopes of achieving **10c**. The former occurrence indicates that additional oxygen atoms cannot be accomodated within the cavity created by the adjacent *peri* *t*-butyl group. On the other hand, the inability of hydroxide ion to displace the thioethoxide group of **10a** may not be of steric consequence (particularly since **10a** could be prepared from **3d** and potassium thioethoxide, a reaction whose steric demands should be quite similar) and may simply be due to an unreactivity of the -SEt functionality to hydroxide ion, analogous to the unreactivity of **4b** to sodium hydroxide.

In hopes of producing **11** as a potential starting point for non-classical antifolates (5), **3e** was treated with ethyl *p*-aminobenzoate. However, a complex mixture of products was obtained which could not be separated completely even after column chromatography.

EXPERIMENTAL

All melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. Ir spectra were recorded as compressed potassium bromide pellets on a Beckman AccuLab 3 spectrophotometer. The pmr spectra were obtained on a Varian EM-360 spectrometer and are reported in parts per million downfield from tetramethylsilane as an internal standard. The spin multiplicities are indicated by the symbols d (doublet) and m (multiplet). Elemental analyses were performed by Het-Chem-Co., Harrisonville, Missouri and Galbraith Laboratories, Knoxville, Tennessee.

General Method of Preparation of the *N*-Acyl-*N'*-(6-chloropyrid-2-yl)hydrazines **2a** and **2c**.

A mixture of **1** (6) (5 g., 34.8 mmoles) and 15 ml. of 88% formic acid or propionic acid was heated at 90-95° for 3.5 hours. After the heating period, 5 ml. of water was added dropwise and the mixture refrigerated. The resulting white crystals of **2a** or **2c** were isolated by filtration, washed with cold water and purified and characterized as shown in Table I.

General Method of Preparation of the *N*-Acyl-*N'*-(6-chloropyrid-2-yl)hydrazines **2b**, **2d** and **2e**.

An equimolar amount of acetyl chloride or pivaloyl chloride was added slowly to a stirred mixture of 1 g. (6.95 mmoles) of **1** (6) in 10 ml. of dry pyridine at 0°. The mixture was then stirred at room temperature for 1.5 hours and then poured, with stirring, into 30 ml. of ice water and refrigerated overnight. The mixture was filtered and the isolated solid (**2b** or **2d**) washed with water, dried, and purified and characterized as indicated in Table I.

Compound **2e** was prepared in an analogous manner except that chloroacetyl chloride in 3 ml. of dry tetrahydrofuran was added to an equimolar amount of **1** (6) being stirred in 25 ml. of dry tetrahydrofuran containing sufficient triethylamine to neutralize the hydrogen chloride liberated during the reaction. After stirring the mixture at 0° for 3 hours, ice water was added and the resultant mixture refrigerated overnight followed by isolation of the product as described above for **2b** and **2d**.

General Method of Preparation of the 5-Substituted- and 3,5-Disubstituted-*s*-triazolo[4,3-*a*]pyridines (**3a-3e**).

Dry **2a-2e** (16 mmoles) in 35 ml. of phosphorus oxychloride was refluxed for 4 hours (20 hours with **2e**) and then stirred at room temperature overnight. The phosphorus oxychloride was removed *in vacuo* and 60 ml. of ice-water was added slowly to the solid residue. The resulting aqueous solution was adjusted to *p*H 6 with concentrated sodium hydroxide under external cooling and then extracted with chloroform (3 x 40 ml.). The combined extracts were dried over anhydrous sodium sulfate and then evaporated on a rotary evaporator to leave a residue (**3a-3e**) which was purified and characterized as described in Table II.

In the preparation of **3c** and **3e** it was necessary to triturate the residue (following removal of the chloroform) with 25 ml. of cold ether-petroleum ether (3:2) in order to realize satisfactory results. On the other hand, treatment of the chloroform extracts of **3e** with decolorizing charcoal prior to its evaporation was required to minimize the complications in the purification of **3e**.

5-Ethoxy-*s*-triazolo[4,3-*a*]pyridine (**4a**).

To a stirring solution of 160 mg. (0.00695 g.-atom) of sodium in 15 ml. of absolute ethanol was added 1 g. (6.5 mmoles) of **3a** and the resulting solution refluxed for 4 hours. The excess ethanol was removed on a rotary evaporator, the residue dissolved in 30 ml. of water and the *p*H adjusted to 6 with concentrated hydrochloric acid. This aqueous solution was extracted with chloroform (3 x 15 ml.), the combined extracts dried over anhydrous sodium sulfate and then evaporated to dryness on a rotary evaporator. The remaining yellow solid was triturated with 20 ml. of ether-petroleum ether (1:1) and purified and characterized as **4a** as described in Table II.

5-Ethylmercapto-*s*-triazolo[4,3-*a*]pyridine (**4b**).

Compound **3a** (1 g., 6.5 mmoles) was added to a stirred solution of 1 g. (17.8 mmoles) of potassium hydroxide and 2 ml. of ethanethiol in 20 ml. of 95% ethanol and this reaction mixture was then heated at 60-70° for 4 hours. After removal of the excess solvents, 20 ml. of water was added to the residue and the the *p*H of the aqueous solution adjusted to *p*H 6 with concentrated hydrochloric acid. The solid which resulted upon cooling was removed by filtration and discarded and the filtrate extracted with chloroform (3 x 15 ml.). The combined extracts were dried over anhydrous sodium sulfate and then evaporated to dryness on a rotary evaporator leaving a yellow oil which was purified and characterized as **4b** as described in Table II.

Table I

N-Acyl- and *N*-Oxalyl-*N'*-(6-chloropyrid-2-yl)hydrazines

Compound	Yield %	M.p. °C (a)	Formula	Analyses % Calculated (Found) C	H	N	Ir (cm^{-1}) (b) ν CO	R	Pmr Data Chemical Shift in δ (c,d) Pyridine	NH
2a	95	191 (AE)	$C_6H_6ClN_3O$	42.00	3.53	24.29	1670	8.06	6.65 (m, 2H)	8.86
				(42.12)	(3.71)	(24.52)			7.48 (m, 1H)	9.60
2b	97	221 (AE)	$C_7H_8ClN_3O$	45.29	4.34	22.64	1665	1.94	6.47 (d of d, 2H)	8.63
				(45.27)	(4.64)	(22.91)			7.52 (t, 1H)	9.75
2c	70	194-195 (AE)	$C_8H_{10}ClN_3O$	48.13	5.05	21.05	1665	1.03 (t)	6.55 (d of d, 2H)	8.60
				(48.27)	(5.11)	(20.79)		2.20 (q)	7.49 (t, 1H)	9.76
2d	89	206-207 (AE)	$C_{10}H_{14}ClN_3O$	52.75	6.20	18.46	1633	1.15	6.56 (d of d, 2H)	8.40
				(53.05)	(6.51)	(18.63)			7.40 (t, 1H)	9.47
2e	82	178-179 (e)	$C_7H_7Cl_2N_3O$	38.20	3.21	19.10	1675	4.16	6.60 (d of d, 2H)	8.85
				(37.98)	(3.49)	(18.90)			7.53 (t, 1H)	10.02
2f	89	140 (AE)	$C_8H_{10}ClN_3O_2$	44.56	4.67	19.49	1720	1.17 (t)	6.57 (m, 2H)	8.63
				(44.31)	(4.35)	(19.45)		4.05 (q)	7.52 (t, 1H)	9.08
2g	94	219 (W)	$C_7H_7ClN_4O_2$	39.17	3.29	26.11	1690	8.02	6.60 (m, 2H)	8.83
				(39.19)	(3.07)	(25.79)	1665		7.75 (t, 1H)	10.27
2h	66	140 (BL)	$C_8H_8ClN_3O_3$	41.84	3.52	18.30	1755	3.80	6.66 (d of d, 2H)	8.94
				(41.76)	(3.60)	(18.16)	1705		7.52 (t, 1H)	9.90
2i	62	131 (B)	$C_9H_{10}ClN_3O_3$	44.36	4.14	17.25	1745	1.35 (t)	6.62 (d of d, 2H)	8.90
				(44.13)	(4.16)	(17.06)	1710	4.28 (q)	7.51 (t, 1H)	9.80

(a) All white crystals; solvent of crystallization: AE, aqueous ethanol; W, washed with methanol, water, methanol and, finally, diethyl ether; BL, benzene-ligroin; B, benzene. (b) As compressed potassium bromide discs. (c) Singlet if not otherwise stated; all NH absorptions were broad singlets and exchangeable with deuterium oxide; d = doublet, t = triplet, q = quartet, m = multiplet. (d) In hexadeuteriodimethylsulfoxide as solvent with tetramethylsilane as an internal standard. (e) Purified by sublimation *in vacuo* (140°/1 mm.).

Table II

5-Substituted- and 3,5-Disubstituted-*s*-triazolo[4,3-*a*]pyridines

Compound	Yield %	M.p. °C (a) (b)	Formula	Analyses % Calculated (Found) C	H	N	Ir (cm^{-1}) (c) ν	Pmr Data Chemical Shifts in δ (d) (e) C-3 Group	Pyridine	C-5 Group
3a	98 (f)	87- 89 (S)	$C_6H_4ClN_3$	46.92 (46.72)	2.63 (2.88)	27.36 (27.51)	1624 (C=C)	9.43	7.40 (m, 2H) 7.80 (d, 1H)	
3b	97	151-153 (S)	$C_7H_6ClN_3$	50.16 (49.93)	3.61 (3.62)	25.07 (25.06)	1615 (C=C)	3.00	7.22 (m, 2H) 7.71 (d of d, 1H)	
3c	90	93-95 (S)	$C_8H_8ClN_3$	52.90 (52.92)	4.44 (4.67)	23.14 (22.90)	1622 (C=C)	1.33 (t) 3.32 (q)	7.13 (m, 2H) 7.47 (d of d, 1H)	
3d	97	125-125 (V)	$C_{10}H_{12}ClN_3$	57.28 (56.90)	5.77 (5.79)	20.04 (19.76)	1620 (C=C)	1.70	7.32 (m, 2H) 7.87 (d of d, 1H)	
3e	100	124-126 (S)	$C_7H_5Cl_2N_3$	41.61 (41.35)	2.50 (2.43)	20.80 (20.99)	1615 (C=C)	5.53	7.40 (m, 2H) 7.87 (d of d, 1H)	
3f	82	215 (W)	$C_6H_5ClN_4$	42.74 (42.51)	2.99 (3.25)	33.24 (32.99)	3300 (NH) 1630 (C=C)	6.11	6.88 (m, 2H) 7.38 (d, 1H)	
3g	93	184 dec. (S)	$C_6H_3BrClN_3$	31.00 (30.98)	1.30 (1.39)	18.08 (17.79)	1635 (C=C)		7.10 (m, 2H) 7.73 (d of d, 1H)	
3i	47	225-226 (W)	$C_7H_5ClN_4O$	42.76 (42.68)	2.56 (2.54)	28.50 (28.40)	3290 (NH) 1685 (C=O)	8.19 8.57	7.39 (m, 2H) 7.90 (d, 1H)	
4a	99	107-108 (B)	$C_8H_9N_3O$	58.88 (59.15)	5.56 (5.76)	25.75 (26.10)	1630 (C=C)	9.08	6.32 (m, 1H) 7.36 (m, 2H)	1.50 (t) 4.42 (q)
4b	95	102/2 mm.	$C_8H_9N_3S$ (g)	51.06 (51.45)	5.31 (5.37)	22.34 (22.29)	1625 (C=C)	8.90	7.08 (m, 3H)	1.35 (t) 3.15 (q)
4c (6)	73	242 dec. (W)	$C_6H_5N_3O$	53.33 (53.16)	3.73 (3.72)	31.10 (30.96)	1650 (C=O)	9.02	5.68 (d, 1H) 6.20 (d, 1H) 7.49 (t, 1H)	
4d	70	138-139 (W)	$C_8H_9N_3O_2S$	45.48 (45.54)	4.30 (4.39)	19.89 (20.01)	1622 (C=C) 1490 (S=O)	9.37	7.52 (m, 2H) 8.07 (d of d, 1H)	1.38 (t) 3.31 (q)
10a	98	89/2 mm.	$C_{12}H_{17}N_3S$	61.25 (60.92)	7.27 (7.37)	17.86 (17.60)	1635 (C=C)	1.77	7.06 (d of d, 2H) 7.64 (d, 1H)	1.32 (t) 3.09 (q)

(a) Crystalline color--all white except **4b** (yellow liquid), **4d** (pale yellow), and **10a** (light yellow liquid). (b) Method of purification: S, sublimation *in vacuo*; V, vacuum distillation using a Kügelrohr distillation apparatus; B, benzene-petroleum ether; W, water. (c) As compressed potassium bromide discs. (d) In hexadeuteriodimethylsulfoxide as solvent (except **10a** which was performed in deuteriochloroform) with tetramethylsilane as an internal standard. (e) Singlet unless stated otherwise; d = doublet, t = triplet, q = quartet, m = multiplet. (f) Compound **3a** has been described previously (7) but was not fully characterized. (g) Possesses 0.5 mole of hydration.

5-Ethylsulfonyl-*s*-triazolo[4,3-*a*]pyridine (**4d**).

Powdered 85% *m*-chloroperoxybenzoic acid (5.5 g., 27 mmoles) was added in small portions to 2.2 g. (12.28 mmoles) of **4b** in 25 ml. of glyme-ether (1:5) with cooling over ice. The yellow mixture was stirred at room temperature overnight and then cooled in a refrigerator. The resulting yellow solid was collected by filtration and dried to give 3.15 g. of a product that produced an acidic solution when dissolved in water and appeared to be a *m*-chlorobenzoate salt. Therefore, this solid was shaken in 90 ml. of saturated sodium bicarbonate solution until no carbon dioxide was evolved and then extracted with chloroform (4 x 30 ml.). The combined extracts were dried over anhydrous sodium sulfate and then concentrated on a rotary evaporator. The residue was then poured into 100 ml. of stirred ether-petroleum ether (1:3) and this mixture chilled to produce pale yellow crystals which were isolated by filtration and purified and characterized as **4d** as detailed in Table II.

s-Triazolo[4,3-*a*]pyridin-5(1*H*)one (**6**).

A solution of 1 g. (4.75 mmoles) of **4d** and 2 g. of potassium hydroxide in 20 ml. of water was heated at 90-95° for 3.5 hours. The hot solution was filtered and neutralized with glacial acetic acid. After cooling, the resulting white precipitate was collected by filtration and purified and characterized as **6** (**4c**) as shown in Table II.

3-Amino-5-chloro-*s*-triazolo[4,3-*a*]pyridine (**3f**).

To a stirred, chilled suspension of 1.5 g. (10.4 mmoles) of **1** in 50 ml. of anhydrous 2-propanol was added, dropwise, a solution of 1.16 g. (11 mmoles) of cyanogen bromide in 20 ml. of anhydrous 2-propanol. The mixture was then heated at 70° for 1.5 hours, cooled and the hydrobromide salt which resulted (2.55 g.) was isolated by filtration and dissolved in 60 ml. of water. Upon adjusting the *p*H to 7 with sodium hydroxide solution and cooling this solution, crude **3f** precipitated and was obtained by filtration and purified and characterized as **3f** as shown in Table II.

7-Chloroimidazo[1,2-*b*]-*s*-triazolo[4,3-*a*]pyridine (**7**).

To a stirred suspension of 1.1 g. (6.5 mmoles) of **3f** in 30 ml. of water was added 2.6 g. (2 ml., 13 mmoles) of bromoacetaldehyde diethyl acetal and the resulting mixture refluxed for 4 hours. The homogeneous solution was cooled and its *p*H adjusted to 7 with solid sodium hydroxide. This dark solution was extracted with chloroform (4 x 20 ml.), the combined chloroform extracts dried over anhydrous sodium sulfate and then evaporated to dryness on a rotary evaporator to leave a residue which was sublimed *in vacuo* to render analytically pure white crystals of **7** (760 mg., 60.8%), m.p. 123-126°; ^{1}H nmr (hexadeuteriodimethylsulfoxide): δ 7.02 (d of d, 1 H), 7.45 (m, 3 H), 7.90 (d, 1 H); ir: 1635 (C=C) cm^{-1}.

Anal. Calcd. for $C_8H_5ClN_4$: C, 49.88; H, 2.62; N, 29.09. Found: C, 50.00; H, 2.70; N, 28.89.

Di(*s*-triazolo[4,3-*a*]pyrid-5-yl)sulfide (**8**).

A mixture of 1 g. (6.5 mmoles) of **3a** and 700 mg. (9.2 mmoles) of thiourea in 40 ml. of 2-propanol was refluxed for 12 hours and then stored at room temperature for 2 days. The resulting mixture was chilled and the yellow crystals which precipitated were collected, dried (740 mg., 75%) and recrystallized from aqueous ethanol to give **9** as yellow crystals, m.p. 272-273° dec.; ^{1}H nmr (deuterium oxide/deuterium chloride): δ 8.16 (m, 3 H), 9.48 (s, 1 H); ir: 3070 (aromatic CH), 1650 (C=C) cm^{-1}.

Anal. Calcd. for $C_{12}H_8N_6S$: C, 53.72; H, 3.01; N, 31.33. Found: C, 53.67; H, 3.07; N, 31.19.

3-Bromo-5-chloro-*s*-triazolo[4,3-*a*]pyridine (**3g**).

Bromine (8 ml.) was added slowly to a cold solution of 1.5 g. (9.8 mmoles) of **3a** in 20 ml. of methanol and the mixture was stirred at room temperature overnight. Water (10 ml.) was added and the mixture was heated on a steam bath to remove the excess bromine after which time the orange colored solution was cooled. The crystals which precipitated were obtained by filtration, suspended in 50 ml. of water and the *p*H carefully adjusted to 10-11 with concentrated sodium hydroxide solution. After stirring the resultant solution for several hours at room temperature, the nearly white solid which precipitated was collected by filtration and purified and characterized as **3g** as outlined in Table II.

5-Chloro-*s*-triazolo[4,3-*a*]pyridine-3-carboxamide (**3i**).

A mixture of 1 g. (4.3 mmoles) of **3g** and 462 mg. (5.16 mmoles) of cuprous cyanide in 1 ml. of dimethylformamide was heated at 150° for 2.5 hours. The dark mixture was cooled and 15 ml. of cold water containing 850 mg. (17.2 mmoles) of sodium cyanide was added and mixed thoroughly. This mixture was then extracted with benzene (4 x 15 ml.), the combined extracts dried over anhydrous sodium sulfate and evaporated on a rotary evaporator leaving a white solid which was recrystallized from benzene-petroleum ether to give 420 mg. (54.7%) of white crystals of **3h**, m.p. 177-179°; ^{1}H nmr (hexadeuteriodimethylsulfoxide): δ 7.61 (m, 2 H), 8.12 (d of d, 1 H); ir: 2240 (CN) cm^{-1}. Numerous attempts to obtain satisfactory microanalytical data for this chromatographically pure substance failed.

Powdered **3h** (500 mg., 2.8 mmoles) thus obtained was suspended in a mixture of 5 ml. of 25% aqueous ethanol and 1 ml. of 30% hydrogen peroxide and to this was added 1 ml. of 25% aqueous potassium hydroxide solution followed by stirring at room temperature for 4 hours. Following refrigeration of the solution overnight, the precipitated white solid was collected and purified and characterized as **3i** as described in Table II.

N-Carboethoxy-*N'*-(6-chloropyrid-2-yl)hydrazine (**2f**).

Finely powdered **1** (6) (2 g., 13.9 mmoles) and 1.99 g. (2 ml., 20.1 mmoles) of ethyl cyanoformate were heated together in an oil bath. When the temperature reached 80°, a reaction occurred in which all of the solid material dissolved and then a white solid quickly formed. The reaction was cooled, the solid collected by filtration, washed with water, and purified and characterized as **2f** as described in Table I.

N-Oxamyl-*N'*-(6-chloropyrid-2-yl)hydrazine (**2g**).

A mixture of 2 g. (13.9 mmoles) of **1** (6) and 1.63 g. (14 mmoles) of ethyl oxamate was fused by heating in an oil bath. When the temperature reached 130°, a clear melt formed and as the temperature was increased to 150° a white solid was deposited. The mixture was then heated at 160° for 10 minutes and cooled. The resulting solid was pulverized and suspended in 60 ml. of stirred methanol for 1 hour. The white solid was collected by filtration, washed with methanol and dried to afford **2g** which was purified and characterized as presented in Table I.

N-Methoxyoxalyl-*N'*-(6-chloropyrid-2-yl)hydrazine (**2h**) and Oxalic Acid 1,2-*Bis*-[2-(6-chloropyrid-2-yl)hydrazide] (**9**).

A mixture of 1.5 g. (10.5 mmoles) of **1** (6) and 1.5 g. (12.7 mmoles) of dimethyl oxalate was carefully heated in an oil bath. A clear solution formed at 80-85° followed subsequently by precipitate formation. The mixture was further heated to 100°, cooled and the residue suspended in petroleum ether, triturated well, filtered and the isolated solid washed with ether. This white material was suspended in 50 ml. of chloroform and stirred at room temperature for 2 hours followed by filtration to obtain a white solid which was washed with chloroform and dried to give **9** (745 mg., 20.8%) recrystallizable from dimethylformamide, m.p. 298°

dec.; ir: 3320 (NH), 3250 (NH), 1700 (C=O), 1620 (C=C) cm^{-1}.

Anal. Calcd. for $C_{12}H_{10}Cl_2N_6O_2$: C, 42.24; H, 2.96; N, 24.64. Found: C, 42.22; H, 2.92; N, 24.62.

Evaporation of the chloroform filtrate remaining from isolation of **9** gave **2h** as a residue which was purified and characterized as described in Table I.

1-Ethyloxalyl-2-(6-chloropyrid-2-yl)hydrazine (**2i**).

Compound **2i** (see Table I) was prepared in a manner analogous to that for **2h** using 2 g. (13.9 mmoles) of **1** (6) and 4 g. (27.3 mmoles) of diethyl oxalate.

3-*t*-Butyl-5-ethylthio-*s*-triazolo[4,3-*a*]pyridine (**10a**).

A solution of 7.7 g. (36.7 mmoles) of **3d** in 15 ml. of ethanol was added to a stirred solution of 11 ml. of ethanethiol and 5.8 g. (103 mmoles) of potassium hydroxide in 80 ml. of ethanol. The mixture was refluxed for 3 hours, cooled, and then neutralized with acetic acid. After evaporating this solution to dryness on a rotary evaporator, the residue was mixed with 80 ml. of water and extracted with chloroform (3 x 40 ml.). The combined extracts were dried over anhydrous magnesium sulfate and evaporated on a rotary evaporator to leave **10a** as an orange colored oil which was purified and characterized as detailed in Table II.

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