PREPARATION OF PYRAZOLO[1,5-a]PYRIDINE AND [1,2,4]TRIAZOLO[1,5-a]PYRIDINE DERIVATIVES FROM 1,6-DIAMINOPYRIDINE-2-THIONES

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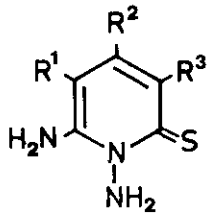
Abstract - The 1,6-diaminopyridine-2-thiones (1a and 1b) react with α-halocarbonyl compounds to give the pyrido [2,1-b][1,3,4]thiadiazinium-salts (2) which undergo base-catalyzed ring-contraction to give the pyrazolo[1,5-a]pyridines (3) or (4). The reactions of the N-amino-heterocycles (1a and 1b) with nitriles lead directly to [1,2,4]triazolo-[1,5-a]pyridines (5).

As a part of an investigation on the synthesis of fused heterocycles from N-aminoheterocycles[1], we have engaged in the preparation of bridgehead nitrogen heterocycles which contain the pyrazolo or [1,2,4]triazolo moiety. In this context, we have reported the preparation of pyrazolo[1,5-a]pyridines from N-aminoazonium salts and substituted acetonitriles[2] or 1,3-dicarbonyl compounds[3], and [1,2,4]triazolo[1,5-a]pyridines from N-amino-2-pyridones and nitriles[4].

The synthesis of fused heterocycles which contain the pyrazolo or [1,2,4]triazolo moiety has continued to attract interest because of their biological activity . Synthesis of pyrazolo[1,5-a]pyridines involve reactions of N-aminopyridinium salts with 1,3-dicarbonyl compounds[5,6], acylating agents[7-9], or activated acetylenic bonds[10-14], and of alkylidenedihydropyridines[15,16]. [1,2,4]Triazolo-[1,5-a]pyridines have been synthesized from 2-aminopyridines by reaction with nitriles[17-19] or hydroxylamine derivatives[20-22].

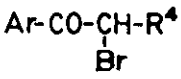
We now describe new general methods for the preparation of some derivatives of the pyrazolo[1,5-a]pyridine and [1,2,4]triazolo[1,5-a]pyridine ring systems. Our approach for the preparation of pyrazolo[1,5-a]pyridines is based on the reaction of the appropriate N-aminoheterocycle, which is conveniently functionalized by a thiocarbonyl and an amino group in the two adjacent positions to the endocyclic nitrogen atom, with α-halocarbonyl compounds to give fused [1,3,4]thiadiazine derivatives which lead to the desired fused pyrazoles by ring contraction. Preparation of [1,2,4]triazolo[1,5-a]pyridines is achieved by reaction of N-aminoheterocycles with nitriles under acid catalysis.



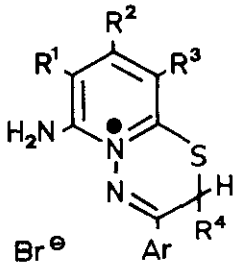
(1)

(1a) R^1=COOEt, R^2= Ph, R^3=H

(1b) R^1=CN, R^2-R^3= -$(CH_2)_4$-

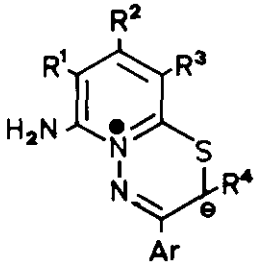


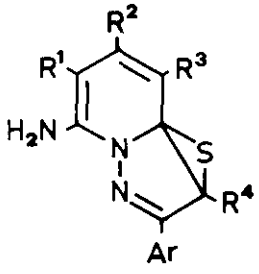
R^4= H or Me



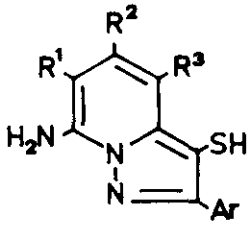
$Br^{\ominus}$ Ar (2)

Et_3N

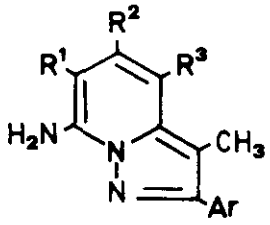




R^4= H | R^4= CH_3



(3)



(4)

Pyrazolo [1,5-a] pyridines

1,6-Diaminopyridine-2-thiones (1a and 1b), themselves readily available from hydrazine and 6-amino-5-ethoxycarbonyl-4-phenylthiopyran-2-thione or 6-amino-5-cyano-3,4-tetramethylenethiopyran-2-thione respectively[23], react with phenacyl bromides or α-bromopropiophenone in ethanol at reflux temperature for 10 h to give the pyrido [2,1-b][1,3,4]thiadiazinium bromides (2) as yellow crystals in moderate to good yields (51-74%) (Table 1). In compounds (2b),(2c),(2d),(2f) and (2g), the S-CH_2- group appears as a singlet at δ 4.2-4.4 ppm, whereas in compounds (2a) and (2e) the methyl group at position 2 appears at δ 1.6 ppm as a doublet and the methine proton appears at δ 4.8-5.7 ppm as a quartet. The most characteristic peaks in the mass spectra are due to the fragments [Ar-CN] and [M^+-HBr-S], which is the base peak.

When ethanolic solutions of compounds (2b),(2c),(2d),(2f) and (2g) are refluxed in the presence of triethylamine for 15 min, these compounds undergo ring-contraction to give the corresponding pyrazolo[1,5-a]pyridines (3) in good yield. However, under similar conditions, compounds (2a) and (2e) undergo sulphur extrusion to give (4). We believe that the conversion of the bicyclic salts (2) into the corresponding pyrazolo[1,5-a]pyridine (3) or (4) is similar to for the base- catalyzed rearrangement of 6H-[1,3,4]thiadiazines into pyrazoles.[24].

The bicyclic salts (2) in basic medium yield the heteroaromatic betaines and their valence isomers with the thiirane ring. In the case of R^4=H, desulfurization occurs predominantly to give (4), however, when $R^4 \neq H$ the pyrazolo[1,5-a]pyridines (3) are isolated. The ^{1}H-nmr of compounds (4) show a signal due to the methyl group at δ 2.4 ppm as a singlet. The mass spectra of compounds (3) show the expected molecular ion and fragments at [M^+-32], as the base peak, and at m/z [Ar-CN]. In compounds (4), the molecular ion is also the base peak.

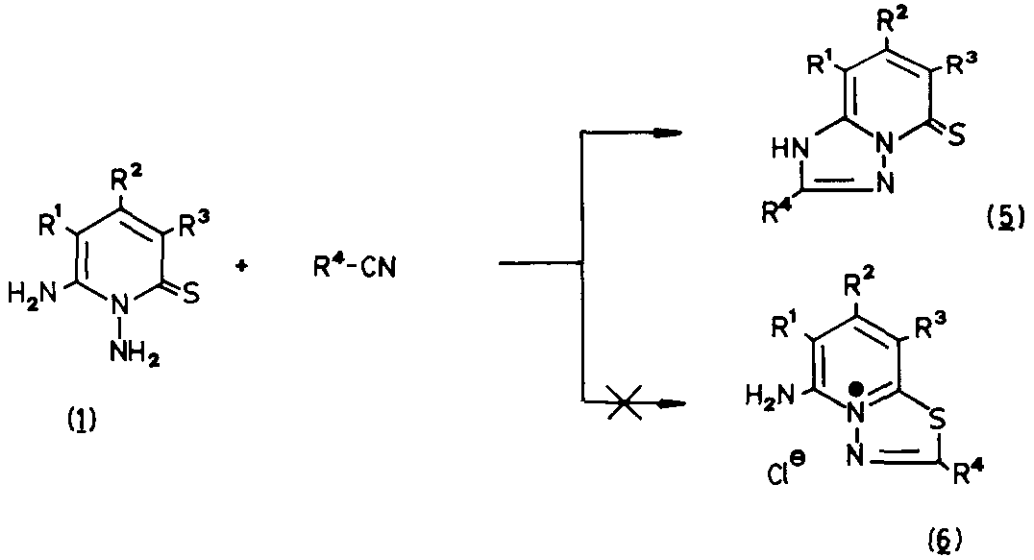


Table 1. Preparation of Pyrido[2,1-b][1,3,4]thiadiazinium Bromides 2, and Pyrazolo[1,5-a]pyridines 3 and 4.

Entry	R^1	R^2	R^3	R^4	Ar	mp(°C)	Yield (%)	Found C	Found H	Found N	Molecular Formula	Required C	Required H	Required N
2a	COOEt	C_6H_5	H	CH_3	C_6H_5	197	53	57.23	4.38	8.57	$C_{23}H_{22}BrN_3O_2S$	57.03	4.58	8.67
2b	COOEt	C_6H_5	H	H	4-$CH_3O.C_6H_4$	178	70	55.18	4.23	8.43	$C_{23}H_{22}BrN_3O_3S$	55.20	4.43	8.40
2c	COOEt	C_6H_5	H	H	4-Br.C_6H_4	189	74	48.12	3.30	7.55	$C_{22}H_{19}Br_2N_3O_2S$	48.11	3.49	7.65
2d	COOEt	C_6H_5	H	H	p-C_6H_5-C_6H_4	182	72	61.57	4.25	7.70	$C_{28}H_{24}BrN_3O_2S$	61.54	4.43	7.69
2e	CN	-$(CH_2)_4$-		CH_3	C_6H_5	199	50	54.87	4.49	13.52	$C_{19}H_{19}BrN_4S$	54.94	4.61	13.49
2f	CN	-$(CH_2)_4$-		H	4-Br.C_6H_4	246	51	44.89	3.25	11.72	$C_{18}H_{16}Br_2N_4S$	45.02	3.36	11.67
2g	CN	-$(CH_2)_4$-		H	p-C_6H_5-C_6H_4	195	52	60.22	4.46	11.49	$C_{24}H_{21}BrN_4S$	60.38	4.43	11.73
3a	COOEt	C_6H_5	H		4-$CH_3O.C_6H_4$	238	69	65.67	5.13	10.15	$C_{23}H_{21}N_3O_3S$	65.85	5.05	10.02
3b	COOEt	C_6H_5	H		4-Br.C_6H_4	272	95	56.50	3.81	8.93	$C_{22}H_{18}BrN_3O_2S$	56.42	3.87	8.97
3c	COOEt	C_6H_5	H		p-C_6H_5-C_6H_4	250	92	72.34	4.78	9.15	$C_{28}H_{23}N_3O_2S$	72.24	4.98	9.02
3d	CN	-$(CH_2)_4$-			4-Br.C_6H_4	306	80	54.32	3.73	14.27	$C_{18}H_{15}BrN_4S$	54.14	3.79	14.03
3e	CN	-$(CH_2)_4$-			p-C_6H_5-C_6H_4	316	78	72.60	5.17	14.12	$C_{24}H_{20}N_4S$	72.70	5.08	14.13
4a	COOEt	C_6H_5	H		C_6H_5	144	73	74.20	5.60	11.16	$C_{23}H_{21}N_3O_2$	74.37	5.70	11.31
4b	CN	-$(CH_2)_4$-			C_6H_5	223	75	75.39	5.86	18.46	$C_{19}H_{18}N_4$	75.47	6.00	18.53

Table 2. Preparation of 1H-[1,2,4]Triazolo[1,5-a]pyridine-5-thiones (5).

Entry	R^1	R^2	R^3	R^4	mp(°C)	Yield (%)	Found C	Found H	Found N	Molecular Formula	Required C	Required H	Required N
a	COOEt	C_6H_5	H	4-CH_3.C_6H_4	203-206	73	67.69	4.79	10.69	$C_{22}H_{19}N_3O_2S$	67.85	4.92	10.79
b	COOEt	C_6H_5	H	CH_3	198-200	76	61.43	4.65	13.29	$C_{16}H_{15}N_3O_2S$	61.32	4.82	13.41
c	CN	$-(CH_2)_4-$		4-CH_3.C_6H_4	233-235	55	67.47	5.12	17.59	$C_{18}H_{16}N_4S$	67.47	5.03	17.50
d	CN	$-(CH_2)_4-$		4-CH_3O.C_6H_4	235-236	64	64.50	4.59	16.70	$C_{18}H_{16}N_4OS$	64.27	4.79	16.65
e	CN	$-(CH_2)_4-$		C_6H_5	240-242	65	66.91	4.59	18.12	$C_{17}H_{14}N_4S$	66.64	4.61	18.29
f	CN	$-(CH_2)_4-$		4-Cl.C_6H_4	248-250	61	60.00	3.90	16.36	$C_{17}H_{13}ClN_4S$	59.91	3.84	16.44
g	CN	$-(CH_2)_4-$		4-NO_2.C_6H_4	255-257	69	58.29	3.89	19.71	$C_{17}H_{13}N_5O_2S$	58.11	3.73	19.93
h	CN	$-(CH_2)_4-$		CH_3	226-227	82	59.20	4.77	22.75	$C_{12}H_{12}N_4S$	58.99	4.95	22.93
i	CN	$-(CH_2)_4-$		H	235-237	71	57.52	4.20	24.14	$C_{11}H_{10}N_4S$	57.37	4.38	24.33

[1,2,4]Triazolo[1,5-a]pyridines

The N-Aminoheterocycles (1a) and (1b), react with nitriles in the presence of hydrogen chloride to give the corresponding [1,2,4]triazolo[1,5-a]pyridine-5-thiones (5) as yellow crystalline solids in moderate to good yields (55-82%) (Table 2). The reaction is equally applicable for aromatic nitriles when the aromatic ring is substituted by either electron-donating or electron- withdrawing groups, as well as aliphatic nitriles. The N-aminopyridine-2-thiones (1) and 1-amino-4,6-diphenylpyridine-2-thione, exhibit stricking differences in their reactions toward nitriles, because the former leads to [1,2,4]triazolo[1,5-a]pyridines (5), whereas the latter leads to [1,3,4]thiadiazolo[3,2-a]pyridinium salts[25] (6). On the other hand, compound (1b) reacts with ethyl orthoformate at 120°C for 12 h to give the [1,2,4]triazolo[1,5-a]pyridine-5- thione (5i) (R^4 = H) in 71% yield. Compound (1a) under similar reaction conditions leads to the N-ethoxymethylene amino derivative, however, attempts to cyclize into (5) failed. We believe that the conversion 1⟶5 involves addition of the N-amino group to the C≡N triple bond to form the not isolated intermediate N-heteroarylamidine which undergoes cyclization followed by elimination of ammonia to give (5).

Table 3. Spectral Data of Compounds 2, 3, 4 and 5.

Compound No	Ir (cm^{-1})	^{1}H-Nmr (ppm)	Ms m/z(%)
2a	3375,3154,1687,1625,1602, 1562,1517,1285,1245,1163, 1141,1111,1093,1070,1001, 864,777,769,698,692.	9.0(2H,s), 8.7-7.4 (10H,m), 7.1(1H,s), 5.7(1H,q,J=7Hz), 4.15(2H,q,J=7Hz), 1.6(3H,d,J=7Hz), 0.9(3H,t,J=7Hz).	404(12),403(3),372(17) 371(100),326(20),325(3) 298(2),222(22),194(16) 116(10),104(31),103(16) 77(40).
2b	3309,3279,1704,1625,1608, 1574,1557,1523,1514,1334, 1278,1257,1234,1190,1138, 1120,1026,993,856,846, 827,763,721,698,	8.75(2H,s), 7.8-7.2 (6H,m), 4.55(2H,s), 4.0(2H,q,J=7Hz), 3.5(3H,s), 0.95(3H,t, J=7Hz).	420(26),419(89)388(26) 387(100),255(5),254(5), 242(7),241(10),240(46), 134(30),133(22),107(10) 77(25).

Table 3 (Continuation)

2c	3381,3250,1693,1625,1596, 1568,1523,1330,1279,1251, 1160,1138,1059,1010,932, 912,847,837,800,768,702.	8.3-7.4(9H,m), 7.2(1H,s),4.4(2H,s) 4.15(2H,q,J=7Hz) 0.85(3H,t,J=7Hz).	470(14),469(63),468(19) 467(58),437(100),435 (30),255(12),241(14), 240(75),184(18),182(16) 157(21),155(18),77(49).
2d	3381,3267,1693,1625,1608, 1562,1517,1421,1336,1257, 1206,1138,1075,1002,858, 843,796,758,723,696.	8.2-7.25(14H,m), 7.0(1H,s),4.4(2H,s) 4.1(2H,q,J=7Hz) 0.75(3H,t,J=7Hz).	466(3),465(5),434(30), 433(100),255(8),254(7), 241(10),240(20),180(29) 179(41),153(29),152(42, 77(24).
2e	3296,3211,2226,1625,1602, 1551,1410,1302,1245,1200, 1047,1002,952,883,775, 747,690.	9.3(2H,s),8.3-7.2 (5H,m), 4.8(1H,q, J=7Hz),3.1~2.7(4H,m) 2.1-1.8(4H,m), 1.6(3H,d,J=7Hz).	335(11),334(5),303(26), 302(100),287(5),286(5), 199(10),171(20),130(10) 104(15),103(10).
2f	3440,3330,3080,2226,1620, 1591,1578,1543,1319,1251, 1230,1176,1070,1007,927, 848,808,651.	8.2-7.4(6H,m) 4.25(2H,s), 3.2-2.6(4H,m), 2.15-1.8(4H,m).	401(2),400(6),399(2), 398(6),369(22),368(97), 367(26),366(100),184 (48),183(24),182(24), 181(13),172(20),171(14).
2g	3443,3307,2219,1628,1608, 1548,1489,1313,1257,1176, 1006,860,844,826,767,696.	8.35-7.4(11H,m) 4.2(2H,s), 3.1-2.5(4H,m), 2.1-1.6(4H,m).	397(2),396(5),365(24), 364(100),186(3),185(7), 180(34),179(34),173(5), 172(5).
3a	3454,3324,1670,1610,1589, 1527,1497,1296,1280,1248, 1201,1171,1105,1032,908, 833,792,769,698.	8.0(2H,d,J=9Hz) 7.6-7.2(7H,m), 6.9(2H,d,J=9Hz) 6.6(1H,s), 4.05(2H,q J=7Hz), 3.8(3H,s) 0.75(3H,t,J=7Hz).	419(M^+,8),418(10),387 (100),386(5),373(5),372 (13),371(42),342(25), 341(85),285(7),134(13), 133(12),77(25).
3b	3449,3318,1670,1610,1589, 1410,1286,1200,1166,1070, 1002,826,792,775,724,698.	7.85-7.35(9H,m) 6.9(1H,s), 4.1(2H,q,J=7Hz) 0.8(3H,t,J=7Hz).	469(M^++2,65),468(17), 467(M^+,62),466(13), 437(97),435(100),423 (25),421(24),184(22), 182(17),157(14),155(10) 77(36).

Table 3 (Continuation)

3c	3454,3324,1676,1613,1585, 1307,1291,1211,1163,1101, 1028,1006,842,792,740,698	8.2-7.2(14H,m) 6.75(1H,s), 3.95(2H, q,J=7Hz),0.65(3H,t, J=7Hz).	465(M^+,13), 464(4), 433(100),419(4),388(28) 387(85),180(41),179(75) 153(63),152(97),77(64).
3d	3443,3335,2208,1630,1591, 1263,1072,1012,835,745, 742.	8.5-7.3(6H,m) 3.4-2.8(4H,m) 2.1-1.8(4H,m).	400(M^++2,3),398(M^+,3) 368(99),366(100),184 (10),183(10),182(6), 157(14),155(13),104(15).
3e	3449,3330,2208,1625,1597, 1489,1296,1268,1177,1109, 1075,1007,843,769,744,696.	8.2-7.2(11H,m) 3.3-2.7(4H,m) 2.1-1.9(4H,m).	396(M^+,3),364(96),363 (10),184(11),180(39), 179(64),153(28),152 (100),104(10).
4a	3460,3330,1670,1626,1595, 1529,1350,1317,1279,1232, 1207,1157,1078,1030,1014, 916,883,791,762,700.	8.2-7.3(12H,m) 6.85(1H,s), 4.05(2H, q,J=7Hz), 2.4(3H,s) 0.75(3H,t,J=7Hz).	371(M^+,100),326(19), 325(75),324(11),298(10) 222(26),194(10),104(6), 77(16).
4b	3437,3318,2203,1630,1599 1579,1363,1354,1327,1296 1273,1182,1142,1080,1010, 864,773,698.	7.6-7.2(7H,m) 3.4-2.8(4H,m) 2.4(3H,s),2.1-1.8 (4H,m)	302(M^+,100),274(17) 198(10),171(28),130(12) 116(11),104(14),103(10).
5a	3369,1715,1625,1579,1545, 1302,1268,1189,1092,1030, 962,866,775,718,701.	9.25(1H,s),8.7-7.6 (9H,m), 6.9(1H,s), 4.2(2H,q), 2.55(3H,s) 0.85(3H,t).	389(M^+,2),388(2),317 (100),316(99),200(68), 199(24),172(31),140(62) 118(50),117(46),91(63), 77(36).
5b	3269,1710,1625,1591,1551, 1466,1285,1223,1183,1092, 1019,996,940,860,798,781, 735,707.	8.25(1H,s), 7.8-7.5 (5H,m), 6.8(1H,s) 4.25(2H,q,J=7Hz), 3.05(3H,s), 0.85(3H,t,J=7Hz).	313(M^+,20),241(100), 240(28),200(32),199(11) 172(25),140(26),77(11).
5c	3375,2223,1635,1556,1496, 1290,1270,1177,1124,1031, 971,953,864,804,740,717, 707.	8.15(2H,d,J=9Hz), 7.9(1H,s), 7.6(2H,d, J=9Hz), 3.2-2.8(4H,m) 2.5(3H,s), 2.2-1.9 (4H,m).	320(M^+,76),319(25), 205(28),204(22),203(26) 202(86),175(13),118(55) 117(100),91(42).

Table 3 (Continuation)

5d	3352,2225,1636,1602,1557, 1393,1365,1313,1298,1255, 1182,1124,1022,972,954, 864,823,738,707,686,669.	8.2(2H,d,J=9Hz) 7.8(1H,s), 7.2(2H,d, J=9Hz), 4.0(3H,s), 3.2-2.8(4H,m), 2.2-1.9(4H,m).	336(M^+,15),335(5), 205(15),204(11),202(21) 134(21),133(100),107 (33).
5e	3352,2225,1636,1596,1551, 1377,1344,1294,1267,1180, 723,690.	8.3-7.7(6H,m) 3.3-2.8(4H,m) 2.3-1.9(4H,m).	306(M^+,98),305(34), 205(13),204(13),203(25) 202(82),143(16),104(58) 103(100),77(45).
5f	3352,2231,1636,1591,1557, 1347,1296,1268,1177,1087, 1030,1013,973,951,928, 866,741,707.	8.2(2H,d,J=9Hz) 7.9(1H,s), 7.7(2H,d, J=9Hz), 3.2-2.8(4H,m) 2.2-1.8(4H,m).	342(M^++2,6),340(M^+,14), 205(28),204(20),203(8), 202(24),139(36),138(17) 137(100),113(4),111(9).
5g	3364,2231,1636,1591,1557, 1534,1523,1342,1296,1268, 1177,1121,1036,1013,973, 883,849,752,707.	8.65(2H,d,J=9Hz) 8.40(2H,d,J=9Hz) 7.9(1H,s), 3.35-2.8(4H,m), 2.25-1.9(4H,m).	351(M^+,2),350(2),205 (28),204(19),203(13), 202(54),148(100),143 (10),122(5).
5h	3269,2225,1625,1568,1540, 1381,1302,1251,1223,1200, 1121,1087,1064,1030,990, 900,860,821,775,690.	3.1-2.75(7H,m) 2.1-1.8(4H,m).	244(M^+,100),243(47), 205(18),204(20),203 (18),202(54),175(19), 143(22),55(93).
5i	2225,1613,1557,1291,1234, 1030,1007,928,866,843, 832,764,724.	8.25(1H,s) 2.8-2.5(4H,m) 2.1-1.7(4H,m).	230(M^+,100),229(15), 203(5),202(5),175(10), 143(15).

[a] Obtained as solutions in $CDCl_3$+TFA, except for compounds (2e),(3a),(3c) and (4a) which were obtained in $CDCl_3$, and (2b) in DMSO-d^6.

[b] Recorded at 70 eV.

EXPERIMENTAL

Melting points were obtained on a Kofler hot-stage apparatus and are uncorrected. Ir spectra were run using NaCl plates on a Nicolet FT-5DX spectrophotometer in Nujol emulsions. ^{1}H-Nmr spectra were obtained on a Varian EM-360A spectrometer at 60 MHz. Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Elemental analyses were performed with a Perkin-Elmer 240C instrument.

General Procedure for the Formation of 6-Amino-3-aryl-2H-pyrido[2,1-f][1,3,4]thiadiazin-3-ium Bromides (2). To a well stirred solution of an appropriate 1,6-diaminopyridine-2-thione (1) (2 mmol) in absolute ethanol (15 ml), the corresponding α-bromocarbonyl compound (2 mmol) was added. The reaction mixture was stirred at reflux temperature for 10 h. After cooling, the precipitated solid was separated by filtration, and recrystallised from ethanol to give (2) as yellow prisms (see Table 1).

General Procedure for the Formation of 7-Amino-2-arylpyrazolo[1,5-a]pyridines (3) and (4). To a solution of an appropriate 2H-pyrido[2,1-f][1,3,4]thiadiazinium bromide (2) (2 mmol) in absolute ethanol (15 ml), triethylamine was added. The resultant solution was stirred at reflux temperature for 12 h. After cooling, the precipitated solid was separated by filtration, and recrystallised from ethanol to give (3) or (4) (see Table 1).

General Procedure for the Formation of [1,2,4]Triazolo[1,5-a]pyridine-5-thiones (5) A stream of dry hydrogen chloride gas was passed through a solution of an appropriate nitrile (2 mmol) in dry dioxan (10 ml) for 30 min. Then, a solution of the adequate 1,6-diaminopyridine-2-thione (1) (2 mmol) in the same solvent (10 ml) was added. The stream of hydrogen chloride was continued for 1 h at room temperature. The resultant suspension was stirred at reflux temperature for 2 h. After cooling, the precipitated solid was separated by filtration, washed with cold ethanol, and recrystallised from ethanol-dichloromethane (1/1) to give (5) (see Table 2).

Reaction of 1,6-Diamino-5-Ethoxycarbonyl-4-phenylpyridine-2-thiones (1b) with Ethyl Orthoformate. A mixture of (1b) (2 mmol) and ethyl orthoformiate (10 ml) was heated in an oil bath at 120°C for 12 h. After cooling, the excess of ethyl orthoformiate was removed off under reduced pressure and the residual material was treated with cold methanol. The separated solid was filtered, dried and recrystallised from ethanol-dichloromethane (1/1) to give (5i) as yellow prisms in 71% yield (see Table 2).

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