Synthesis of Imidazo[4,5-*b*]- and [4,5-*c*]pyridines

*Richard W. Middleton and D. George Wibberley**

Department of Pharmacy, University of Aston, Gosta Green, Birmingham B4 7ET, England

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2-Arylimidazo[4,5-*b*]- and [4,5-*c*]pyridines have been prepared by treatment of the appropriate 2,3- or 3,4-diaminopyridine with an aromatic carboxylic acid in the presence of polyphosphoric acid. Other derivatives have been prepared by similar cyclisation of diaminopyridines using triethyl orthoformate, urea, thiophosgene and thiourea and the properties of some *N*-oxides have been investigated. A number of the arylimidazopyridines have been screened for mutagenicity.

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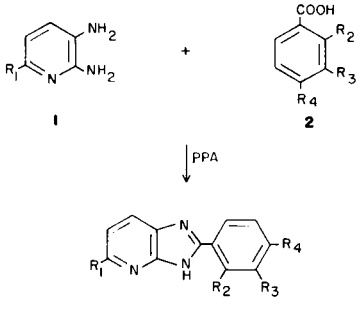
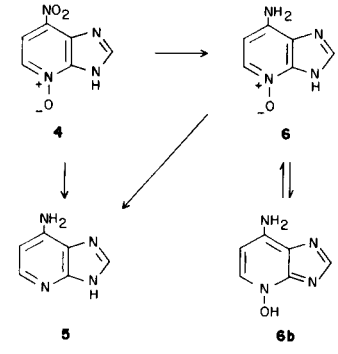
Antiviral (1), rodenticidal (2), antimicrobial (3) and cytotoxic (4) activity has been demonstrated in a number of imidazo[4,5-*b*]- and [4,5-*c*]pyridines. In view of the fact that these ring systems are 1- and 3-deazapurines it seems highly likely that in all these cases the compounds are behaving as purine anti-metabolites. We were interested in preparing a series of such compounds for routine anti-cancer screening tests, but more particularly to study the use of the Ames test as an initial *in vitro* screening test for cytotoxic activity, since the majority of purine anti-metabolites are also mutagenic in this test (5).



1 + 2 → (PPA) → 3

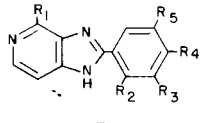
	R^1	R^2	R^3	R^4
a;	H	Cl	H	H
b;	H	H	NO_2	H
c;	H	H	Cl	H
d;	H	H	Br	H
e;	H	H	H	NO_2
f;	H	H	H	Br
g;	NH_2	CH_3	H	H
h;	NH_2	H	NO_2	H
i;	NH_2	H	Cl	H
j;	NH_2	H	Br	H
k;	NH_2	H	H	CH_3
l;	NH_2	H	H	NO_2
m;	NH_2	H	H	Cl
n;	NH_2	H	H	Br

Treatment of the 2,3-diaminopyridine (**1**) with an aromatic acid (**2**) in an excess of polyphosphoric acid at 160-200° for several hours gave good yields of the 2-aryl-imidazo[4,5-*b*]pyridines (**3**). 3*H*-Imidazo[4,5-*b*]pyridine, the related 4-*N*-oxide and the 7-nitro *N*-oxide (**4**) were all



4 → 6; 4 → 5; 6 ⇌ 6b

prepared in high yield by modification of literature methods (6,7). Previous authors (7) have claimed that hydrogenation of the nitro *N*-oxide (**4**) in the presence of Raney nickel yields the amine (**5**). In our hands, however, such a reduction, or a hydrogenation with palladium on charcoal in ethanol, or platinum oxide in water gave 7-amino-3*H*-imidazo[4,5-*b*]pyridine 4-*N*-oxide (**6**) as the sole isolated product and the use of acetic acid and anhydride with palladium charcoal was required for conversion of either the nitro *N*-oxide (**4**) or the amine *N*-oxide



7

	R^1	R^2	R^3	R^4	R^5
a;	H	H	H	H	H
b;	H	OH	H	H	H
c;	H	NO_2	H	H	H
d;	H	H	Cl	H	H
e;	H	H	H	Cl	H
f;	H	H	H	NO_2	H
g;	H	H	H	NH_2	H
h;	Cl	CH_3	H	H	H
i;	Cl	Cl	H	H	H
j;	Cl	H	Cl	H	H
k;	Cl	H	NO_2	H	H
l;	Cl	H	NO_2	H	NO_2
m;	Cl	H	H	CH_3	H
n;	Cl	H	H	Br	H
o;	Cl	H	H	Cl	H
p;	Cl	H	H	NO_2	H

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Table 1

2-Arylimidazo[4,5-*b*]pyridines

Compound No.	Reaction Temp. (°C/hours)	Yield (%)	M.p. (°C)	Crystallisation Solvent	Formula	% Found (Calculated) C	H	N	M⁺ Found (Calculated)	Nmr (δ values)
3a	180/3	62	188-189	ethanol	$C_{12}H_8ClN_3$	62.4 (62.7)	3.4 (3.5)	18.5 (18.3)	229.04121 (a) (229.04067)	7.67 (5H, m, 3'-, 4'-, 5'-, 6'-, 7-H), 7.99 (1H, t, J = 5 Hz, 6-H), 8.85 (1H, d, J = 6 Hz, 5-H)
3b	160/2	89	>300	DMF	$C_{12}H_8N_4O_2$	59.6 (60.0)	3.7 (3.3)	23.6 (23.3)	240.06421 (240.064721)	
3c	180/4	85	287-288	methanol	$C_{12}H_8ClN_3$	62.6 (62.9)	3.4 (3.5)	18.2 (18.3)	229.04097 (a) (229.04067)	
3d	180/3.5	87	>300	ammonium hydroxide/-hydrochloric acid sublimed	$C_{12}H_8BrN_3$	52.5 (52.7)	2.9 (2.9)	15.6 (15.4)	272.99032 (b) (272.99021)	
3e	170/3	74	>300	sublimed	$C_{12}H_8N_4O_2$	60.0 (60.0)	3.2 (3.3)	23.2 (23.3)	240.064370 (240.064721)	
3f	180/3	95	>300	sublimed	$C_{12}H_8BrN_3$	52.6 (52.7)	2.8 (2.9)	15.2 (15.4)	272.9903 (b) (272.99021)	7.95 (4H, m, 2'-, 3'-, 5'-, 6-H), 8.8 (1H, d, J = 6 Hz, 7-H), 8.86 (1H, t, 6-H), 8.95 (1H, d, J = 6 Hz, 5-H)
3g	180/3	53	220-221	water	$C_{13}H_{12}N_4$	69.2 (69.6)	5.3 (5.4)	24.9 (25.0)	224.105990 (224.106191)	
3h	170/2	85	181-183	methanol	$C_{12}H_9N_5O_2$	56.1 (56.5)	3.4 (3.5)	27.1 (27.5)	255.07637 (255.075619)	
3i	180/3	84	>300	ethanol/hydrochloric acid	$C_{12}H_{10}Cl_2N_4$	51.0 (51.2)	3.9 (3.39)	20.3 (19.9)	244.05167 (a) (244.05157)	
3j	200/3	82	>300	ethanol/hydrochloric acid	$C_{12}H_{11}BrCl_2N_4$	39.5 (40.0)	3.0 (3.1)	15.2 (15.5)	288.000991 (b) (288.001110)	
3k	180/3	88	>300	water	$C_{13}H_{12}N_4$	69.5 (69.6)	5.6 (5.4)	25.3 (25.0)	244.10645 (244.106191)	
3l	180/2	78	220-221	DMF	$C_{12}H_9N_5O_2$	56.0 (56.5)	3.2 (3.5)	27.1 (27.5)	255.07599 (255.075619)	
3m	190/2.5	89	>300	ethanol	$C_{12}H_9ClN_4$	58.5 (59.0)	3.6 (3.7)	22.6 (23.0)	244.05113 (a) (244.05157)	
3n	170/3	83	>300	ethanol/hydrochloric acid	$C_{12}H_9BrN_4$				288.000580 (b) (288.001110)	8.02 (1H, d, J = 9 Hz, 6-H), 8.64 (4H, m, 2'-, 3'-, 5'-H), 9.17 (1H, d, J = 9 Hz, 7-H)

(a) M^+ for the Cl^{35} isomer (Cl^{37} also obtained). (b) M^+ for the Br^{79} isomer.

(**6**) into the amine (**5**). The bright orange colour of the amine *N*-oxide is probably due to the presence of the quinonoid tautomer (**6b**). Treatment of 3*H*-imidazo-[4,5-*b*]pyridine 4-*N*-oxide with phosphoryl chloride yielded 5-chloro-3*H*-imidazo[4,5-*b*]pyridine and similar treatment of both the 7-nitro- (**4**) and the 7-amino *N*-oxide (**5**) yielded 5,7-dichloro-3*H*-imidazo[4,5-*b*]pyridine, a compound previously obtained by ring closure of 2,3-diamino-4,6-dichloropyridine (8).

5-Amino-3*H*-imidazo[4,5-*b*]pyridin-2-(1*H*)one and 5-amino-3*H*-imidazo[4,5-*b*]pyridine-2-(1*H*)thione were obtained in good yields by treatment of 2,3,6-triaminopyridine with urea and with either thiophosgene or thiourea.

Treatment of either 3,4-diaminopyridine or 3,4-diamino-2-chloropyridine with an aromatic carboxylic acid in an excess of polyphosphoric acid for several hours at 160-200° gave good yields of the 2-arylimidazo[4,5-*c*]-pyridines (**7**). Similar conditions using formic acid, acetic acid and nicotinic acid yielded the parent 1*H*-imidazo-[4,5-*c*]pyridine, the 2-methyl and the 2,2'-pyridyl derivatives. 3,4-Diaminopyridine on treatment with phosgene or on fusion with urea by a previously reported method (9) yielded 1*H*-imidazo[4,5-*c*]pyridine-2-(3*H*)one. The latter could not be nitrated by the previously reported method (10) but treatment with acetic acid and hydrogen peroxide gave a mono *N*-acetyl derivative of the 4-*N*-oxide.

7-Amino-1*H*-imidazo[4,5-*c*]pyridine and 7-amino-1*H*-imidazo[4,5-*c*]pyridin-2-(3*H*)one were isolated as their hydrochlorides after treatment of 3,4,5-triaminopyridine with triethyl orthoformate and with urea.

Attempts to replace the chloro-substituent in 4-chloro-1*H*-imidazo[4,5-*c*]pyridine by methoxy-, hydroxylamino-, or amino- using methods which has succeeded with 6-chloropurine gave unchanged starting material in all cases.

A full description of the mutagenicity screening methods and results are recorded elswhere (11). Eight of the compounds, all of which contained nitro groups in the phenyl rings, were found to be frame shift mutagens with a pattern of activity similar to that of 2-nitrosofluorene; the 2-(4-nitrophenyl)imidazo[4,5-*c*]pyridine (**7f**) (1) was particularly potent.

Table 2

2-Arylimidazo[4,5-*c*]pyridines

Compound No.	Reaction Temp. (°C/hours)	Yield (%)	M.p. (°C)	Crystallisation Solvent	Formula	% Found (Calculated) C	H	N	M⁺ Found (Calculated)	Nmr (δ values)
7a	180/3.5	90	230-231	water	$C_{12}H_9N_3$	73.4 (73.8)	4.4 (4.6)	21.3 (21.5)	195.07961 (195.079643)	7.2 (3H, m, 3'-, 4'-, 5'- H), 7.57 (2H, m, 2'-, 6'-H), 7.86 (1H, d, J = 7 Hz, 7-H), 8.27 (1H, d, J = 7 Hz, 6-H), 9.02 (1H, s, 4-H)
7b	180/4	72	117-118	ethanol	$C_{12}H_9N_3O$	68.1 (68.3)	4.2 (4.3)	20.1 (19.9)	211.07478 (211.074557)	
7c	180/2	63	145-146	chloroform	$C_{12}H_8N_4O_2$	59.5 (60.0)	3.1 (3.3)	22.9 (23.3)	240.064280 (240.064721)	
7d	180/4	86	>300	ethanol	$C_{12}H_8ClN_3$				229.04073 (a)	7.5 (1H, m, 2'-H), 7.95 (3H, m, 4'-, 5'-, 6'-H), 8.2 (1H, d, J = 7 Hz, 7-H), 8.6 (1H, d, J = 7 Hz, 6-H), 9.45 (1H, s, 4-H)
7e	180/4	86	>300	DMF	$C_{12}H_8ClN_3$				229.04049 (a)	8.03 (4H, m, 2'-, 3'-, 5'-, 6'-H), 8.25 (1H, d, J = 7 Hz, 7-H), 8.67 (1H, d, J = 7 Hz, 6-H)
7f	190/4	87	>300	ethanol/hydrochloric acid	$C_{12}H_{10}Cl_2N_4O_2$	46.0 (46.1)	3.2 (3.2)	17.9 (17.8)	240.065420 (240.064720)	
7g	180/4	80	>300	ethanol	$C_{12}H_{10}N_4$	68.3 (68.6)	4.7 (4.8)	26.5 (26.7)	210.08286 (210.082717)	
7h	170/2	70	110-111	ethanol	$C_{13}H_{10}ClN_3$				245.053710 (c) (245.05337)	2.56 (3H, s, 2' -CH_3), 8.4 (1H, s, J = 6 Hz, 7-H), (245.05337) 8.67 (4H, m, 3'-, 4'-, 5'-, 6' -H), 8.83 (1H, s, J = 6 Hz, 6-H)
7i	200/1	82	104-106	water	$C_{12}H_7Cl_2N_3$	54.3 (54.8)	2.5 (2.7)	15.6 (16.0)	236.00124 (a) (263.00169)	
7j	170/2	87	>300	water	$C_{12}H_7Cl_2N_3$				263.00187 (a) (263.00169)	7.82 (3H, m, 4'-, 5'-, 6' -H), 8.28 (2H, m, 7-H, 2'-H), 8.74 (1H, d, J = 7 Hz, 6-H)
7k	190/2	78	>300	ethanol	$C_{12}H_7ClN_4O_2$				274.026040 (a) (274.025750)	7.92 (1H, d, J = 6 Hz, 7-H), 8.31 (1H, d, J = 7 Hz, 6-H), 8.68 (3H, m, 4'-, 5'-, 6'-H), 9.07 (1H, s, 2-H)
7l	170/2.5	89	>300	ethanol	$C_{12}H_6ClN_5O_4$	44.9 (45.1)	1.7 (1.8)	21.6 (21.9)	319.011520 (a) (319.010820)	
7m	170/2.5	88	243-244	DMF	$C_{13}H_{10}ClN_3$				243.055390 (a) (243.056320)	2.88 (3H, s, 4-CH_3), 8.16 (2H, d, J = 8 Hz, 3'-, 5'-H), 8.75 (2H, d, J = 8 Hz, 2'-, 6'-H), 8.87 (1H, d, 6 Hz, 7-H), 9.31 (1H, d, J = 6 Hz, 6-H)
7n	200/1	89	>300	ethanol	$C_{12}H_7BrClN_3$	46.6 (46.9)	2.3 (2.3)	13.6 (13.7)	306.95175(a,b) (306.95123)	8.05 (4H, M, 2'-, 3'-, 5'-, 6'-H), 8.27 (1H, d, J = 7 Hz, 7-H), 8.67 (1H, d, J = 7 Hz, 6-H)
7o	200/0.5	91	>300	ethanol	$C_{12}H_7Cl_2N_3$	54.5 (54.8)	2.6 (2.7)	15.6 (16.0)		8.15 (1H, d, J = 7 Hz, 7-H), 8.65 (4H, m, 2'-, 3'-, 5'-, 6'-H), 9.1 (1H, d, J = 7 Hz, 6-H)
7p	180/3	82	282-284	DMF	$C_{12}H_7ClN_4O_2$				274 (274)	8.25 (1H, d, J = 7 Hz, 7-H), 8.5 (4H, m, 3'-, 3'-, 5'-, 6'-H), 8.57 (1H, d, J = 6 Hz, 6-H)

(a) M^+ for the Cl^{35} isomer (Cl^{37} also obtained). (b) M^+ for the Br^{79} isomer. (c) M^+ for the Cl^{37} isomer.

EXPERIMENTAL

Spectra were recorded with a Unicam S.P. 200 infrared spectrophotometer, and A.E.I. MS9 mass spectrometer, and a Varian A60-A spectrometer. Melting points are uncorrected and reaction temperatures are those of an external oil bath.

2-Arylimidazo[4,5-*b*]pyridines (**3**).

The 2,3-diaminopyridine (0.01 mole), the aromatic acid (0.01 mole) and polyphosphoric acid (30 g.) were stirred together for the time and temperature recorded in Table 1. The mixture was cooled, neutralised with potassium carbonate and the product crystallised from the stated solvent, with a prior vacuum sublimation where this appeared desirable for purification. The products are listed in Table 1. Satisfactory mass and infrared spectra were additionally obtained.

7-Amino-3*H*-imidazo[4,5-*b*]pyridine 4-*N*-Oxide (**6**).

The nitro *N*-oxide (4) (2.6 g.) was shaken with 5% palladium on charcoal (0.26 g.) in absolute ethanol in the presence of hydrogen at 3 atmospheres for 5 hours at room temperature. The mixture was filtered and the filtrate evaporated *in vacuo* to yield the amine *N*-oxide (1.1 g., 51%) as orange needles, m.p. 247-248° from ethanol. Identical products were obtained using Raney nickel and ethanol or platinum oxide and water; ir (potassium bromide): 3200, 1660, 1530, 1440, 1410, 1360, 1320, 1300, 1220, 820, 660 cm^{-1}; nmr (DMSO-d_6): δ 6.9 (1H, d, J = 8 Hz, 6-H), 7.5 (1H, brs, 7-NH_2), 8.4 (1H, d, J = 8 Hz, 5-H), 8.5 (1H, s, 2-H).

Anal. Calcd. for $C_6H_6N_4O_4$: C, 48.0; H, 4.0; N, 37.3. Found: C, 47.5; H, 4.1; N, 37.0.

7-Amino-3*H*-imidazo[4,5-*b*]pyridine (**5**).

The nitro *N*-oxide (0.6 g.), palladium charcoal (0.6 g.), glacial acetic

acid (130 ml.) and acetic anhydride (10 ml.) were hydrogenated at 3 atmospheres for 6 hours. The solvent was removed *in vacuo* and concentrated hydrochloric acid (0.2 ml.) was added to yield the amine hydrochloride (0.42 g., 74%), colourless plates, m.p. > 300° [lit. (5) m.p. 328°]. Under similar conditions the amine *N*-oxide (6) yielded an identical product in 82% yield; ir (potassium bromide): 3200, 2700, 1660, 1620, 1560, 1510, 1430, 1330, 1320, 1220, 940, 880 cm^{-1}; nmr (DMSO-d_6): δ 6.95 (1H, d, J = 7 Hz, 6-H), 8.21 (1H, d, J = 7 Hz, 5-H), 8.72 (1H, 5, 2-H).

Anal. Calcd. for $C_6H_6N_4$: C, 42.4; H, 4.1; N, 32.9; M, 134.059243. Found: C, 42.2; H, 4.1; N, 32.7; M⁺, 134.059140.

5-Chloro-3*H*-imidazo[4,5-*b*]pyridine.

3-*H*-Imidazo[4,5-*b*]pyridine 4-*N*-oxide (0.3 g.) and phosphoryl chloride (20 ml.) were heated at 100° for 6 hours and the excess phosphoryl chloride was removed *in vacuo*. The residual solid was stirred with crushed ice and ammonia solution and extracted continuously with chloroform for 12 hours to yield the imidazopyridine (0.3 g.), 77% m.p. 257-258° from ethanol; ir (potassium bromide): 1600, 1580, 1380, 1340, 1280, 1220, 1100, 940, 820 cm^{-1}.

Anal. Calcd. for $C_6H_4ClN_3$: C, 47.0; H, 2.6, N, 27.5; M, (Cl^{37}) 155.00642. Found: C, 47.2; H, 2.5; N, 27.3; M+, 144.00625.

5,7-Dichloro-3*H*-imidazo[4,5-*b*]pyridine.

The nitro *N*-oxide (4) (2 g.) and phosphoryl chloride (100 ml.) were heated at 100° for 2.5 hours and the excess phosphoryl chloride was removed *in vacuo*. The residual solid was stirred with crushed ice and an ammonia solution to yield the imidazopyridine as light yellow needles (1.8 g., 86%), m.p. 273-274° from water [lit. (7) m.p. 275°]. Similar treatment of the amine (6) gave the same product, ir (potassium bromide): 3010, 1550, 1440, 1350, 1330, 1250, 1140, 950, 910, 810 cm^{-1}; nmr (DMSO-d_6): δ 8.14 (1H, s, 6-H), 8.93 (1H, s, 2-H).

Anal. Calcd. for $C_6H_3Cl_2{}^{35}N_3$: M, 186.9704 and for $C_6H_3Cl_2{}^{37}N_3$: 190.9645. Found: M⁺, 186.97018 and M⁺, 190.96441.

Treatment of the dichloro compound with alcoholic ammonia in a steel bomb at 100° for 12 hours gave only unchanged starting material.

5-Methyl-3*H*-imidazo[4,5-*b*]pyridin-2-(1*H*)one.

2,3-Diamino-6-methylpyridine dihydrochloride (1 g.) and urea were intimately mixed in a mortar and then heated at 240° (metal bath) for 0.5 hour. The residual solid was washed with cold water (20 ml.) and recrystallised from ethanol to yield the imidazopyridone (7) (0.88 g., 79%), light colourless needles, m.p. 249-250°; ir (potassium bromide): 3500, 3100, 1720, 1620, 1460, 1120, 810, 770, 710 cm^{-1}; nmr (trifluoroacetic acid): δ 2.85 (3H, s, 5-CH_3), 8.6 (1H, d, J = 8 Hz, 6-H), 9.28 (1H, d, J = 8 Hz, 7-H).

Anal. Calcd. for $C_7H_7N_3O$: C, 56.4; H, 4.7; N, 28.2; M, 149.058908. Found: C, 56.4; H, 4.6; N, 28.4; M⁺, 149.058070.

5-Amino-3*H*-imidazo[4,5-*b*]pyridin-2-(1*H*)one.

2,3,6-Triaminopyridine dihydrochloride (1.2 g.) and urea (1.2 g.), were ground together and then heated at 170° (metal bath) for 10 minutes. The residual solid was triturated with water (25 ml.) and the residual brown solid dissolved in hot dilute ammonia solution (charcoal) and precipitated with acetic acid to yield the imidazopyridine (0.8 g., 87%), m.p. > 300°; ir (potassium bromide): 3400, 3150, 1700, 1640, 1600, 1440, 1240, 1040, 1020, 900 cm^{-1}; no suitable solvent was found for the nmr determination.

Anal. Calcd. for $C_6H_6N_4O$: M, 150.054157. Found: M⁺, 150.054470.

Treatment of the imidazopyridine with sodium nitrite with dilute sulphuric acid gave unchanged starting material and not the required 3-*H*-imidazo[4,5-*b*]pyridine-2,5-(1*H*,4*H*)dione.

5-Amino-3*H*-imidazo[4,5-*b*]pyridine-2-(1*H*)thione.

(a)

Thiophosgene (1 ml.) was added dropwise to a stirred solution of 2,3,6-triaminopyridine dihydrochloride (0.6 g.) in concentrated hydrochloric acid (10 ml.) and water (10 ml.). The mixture was stirred for 24 hours and a yellow precipitate removed. The filtrate was basified with ammonia to yield the imidazopyridine-2-(1*H*)thione (0.39 g., 83%, which was purified by dissolution in ammonia solution followed by precipitation with acetic acid.

(b)

The triamine dihydrochloride (2 g.) and thiourea (2 g.) were intimately mixed and heated at 230° for 0.5 hour to yield the same thione, m.p. > 300°, ir (potassium bromide): 3400, 3200, 1640, 1500, 1460, 1350, 1310, 1170, 820, 650 cm^{-1}; nmr (DMSO-d_6): 5.8 (2H, brs, 5-NH_2), 6.25 (1H, d, J = 9 Hz, 6-H), 7.27 (1H, d, J = 9 Hz, 7-H).

2-Arylimidazo[4,5-*c*]pyridines (7).

The 3,4-diaminopyridine (0.01 mole), the aromatic acid (0.01 mole) and polyphosphoric acid (30 g.) were stirred together for the time and temperature recorded in Table 2. The mixture was cooled, neutralised with potassium carbonate to yield the imidazopyridine listed in Table 2. Satisfactory infrared spectra and mass spectral fragmentation pathways were also obtained for the compounds listed.

2-(2-Pyridyl)-1*H*-imidazo[4,5-*c*]pyridine.

Similar reaction with nicotinic acid in place of the benzoic acids yielded the imidazopyridine (0.91 g., 90%), light pink needles, m.p. 219-220° from aqueous ethanol; ir (nujol): 1600, 1580, 1540, 1300, 960, 920, 820, 740, 710 cm^{-1}.

Anal. Calcd. for $C_{11}H_8N_4$: C, 67.3; H, 4.1; N, 28.6; M, 196.074892. Found: C, 67.1; H, 4.1; N, 28.7; M⁺, 196.0746.

7-Amino-1*H*-imidazo[4,5-*c*]pyridine Hydrochloride.

3,4,5-Triaminopyridine hydrochloride (12) (1 g.) and triethyl orthoformate (10 ml.) were heated under reflux with stirring for 3 hours. The solution was evaporated to dryness and triturated with concentrated hydrochloric acid to yield the imidazopyridine hydrochloride (0.8 g., 89%), m.p. > 300°; ir (potassium bromide): 3300, 3000, 1660, 1570, 1460, 1400, 1260, 1130, 1090, 840, 730 cm^{-1}; nmr (DMSO-d_6): 8.2 (1H, s, 6-H), 8.4 (1H, s, 4-H), 8.6 (2H, s, 7-NH_2), 9.1 (1H, s, 2-H).

Anal. Calcd. for $C_6H_7ClN_4$: C, 42.4; H, 4.1; N, 32.9; Calcd. for $C_6H_6N_4$: 134.05901. Found: C, 42.0; H, 3.9; N, 32.5; M⁺, 134.05924.

7-Amino-1*H*-imidazo[4,5-*c*]pyridin-2-(3*H*)one Dihydrochloride.

3,4,5-Triaminopyridine hydrochloride (1 g.) and urea (0.3 g.) were intimately mixed and heated at 320° for 0.5 hours. The residue was boiled with water and filtered to yield the imidazopyridine dihydrochloride (0.85 g., 89%), m.p. > 300° from ethanolic hydrogen chloride; ir 3200, 3000, 1680, 1640, 1570, 1490, 1420, 1230, 1000, 820, 740 cm^{-1}; nmr (trifluoroacetic acid): 8.35 (1H, s, 4-H), 8.23 (1H, s, 6-H).

Anal. Calcd. for $C_6H_8Cl_2N_4O$: C, 32.4; H, 3.6; N, 25.2; Calcd. for $C_6H_6N_4O$: M, 150.05396. Found: C, 32.0; H, 3.5; N, 25.0; M+, 150.05416.

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