Novel Synthesis of Pyrido[1,2-*a*]benzimidazoles *via* Reaction of *N*-Acyl Arylhydroxylamines with Pyridine

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The reduction of 4-chloro-3,5-dinitrobenzonitrile *via* catalytic hydrogenation and/or titanium trichloride produced three successive hydroxylamines **6,7**, and **8** that were fully characterized during complete reduction to the diamine **9**. The nitrohydroxylamine **6** was acetylated to the *mono-N*-acetyl and *bis*-acetyl derivatives **10** and **11** which reacted with pyridine to afford the pyrido[1,2-*a*]benzimidazole **13**. An analoguous series of reactions was executed with 4-chloro-3,5-dinitrobenzotrifluoride to afford the pyrido-[1,2-*a*]benzimidazole **21**. Structure confirmation of **21** was established *via* an x-ray determination. The mechanism of the transformation is discussed.

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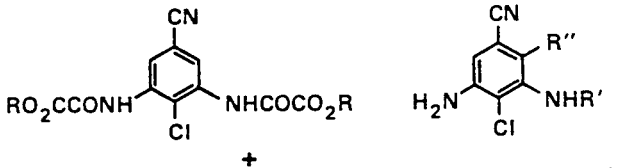
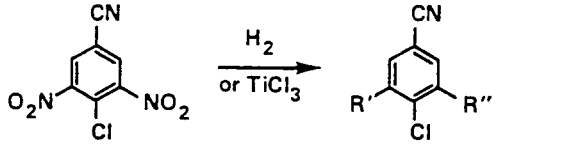
The dioxamate lodoxamide **1** and its ethyl ester **2** have been undergoing development in our research division as potential anti-asthma agents [1]. As part of the program, the synthesis of two possible metabolites, the aminohydroxylamine **3** and the diaminophenol **4**, was initiated (Scheme 1).



1 R = $(HOCH_2)_3\overset{+}{N}H$
2 R = Et
3 R′ = OH, R″ = H
4 R′ = H, R″ = OH

Scheme 1

Several methods of reduction are available [2] for the conversion of nitro compounds to hydroxylamines including aluminum amalgam, diborane, electrochemical, hydrogenation, and sodium hydrosulfide. Careful catalytic hydrogenation [3] of the dinitro compound **5** revealed several intermediates (by tlc) on the way to formation of the diamine **9**. The primary reduction product was identified as the nitrohydroxylamine **6** which could be further reduced to the dihydroxylamine **7**. These two products could also be formed *via* careful reaction with titanium trichloride. Continued reduction of **7** with titanium trichloride afforded the aminohydroxylamine **8** and finally the diamine **9**. If nitroso compounds were formed during the reduction, we were not able to identify or isolate them.



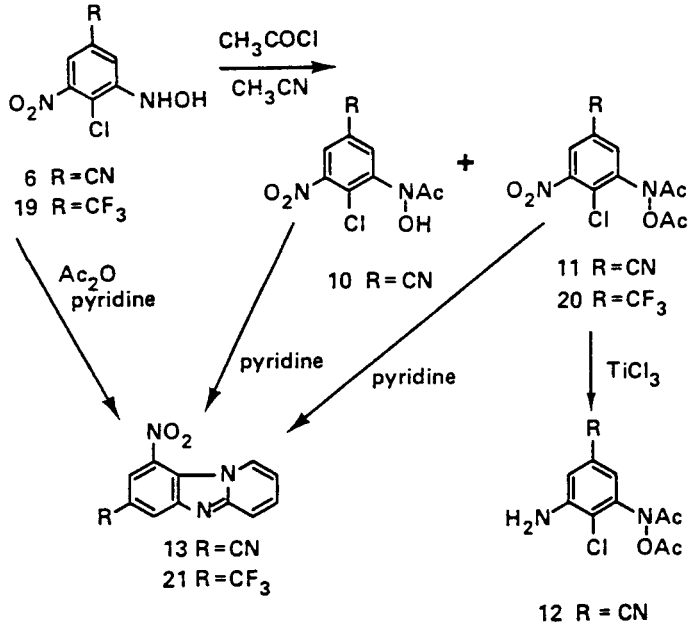
5

6 R′ = NO_2, R″ = NHOH
7 R′ = R″ = NHOH
8 R′ = NHOH, R″ = NH_2
9 R′ = R″ = NH_2

Scheme 2

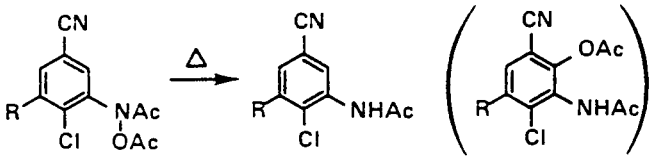
Under acid or thermal conditions the aminohydroxylamine **8** failed to undergo a Bamberger type of rearrangement [4] to the diaminophenol **4**.

Diacyl hydroxylamines have been reported [5] to isomerize very readily to the phenolic derivatives, often precluding the isolation of the former compounds. Thus, we reacted the nitrohydroxylamine **6** with acetyl chloride in acetonitrile to afford first the *N*-acetyl compound **10** and then the diacetylhydroxylamine **11** (Scheme 3). The latter could be reduced to the amine **12** with titanium trichloride.



Scheme 3

Both **11** and **12** failed to rearrange to the appropriate aryl acetates **16** (Scheme 4). After heating **12** in refluxing xylene for 24 hours, 50% was recovered unchanged and a small amount of the acetanilide **15** was isolated. Similarly the nitro compound **11**, in refluxing trichlorobenzene, afforded the acetanilide **14**.



11 R=NO_2 14 R=NO_2 16
12 R=NH_2 15 R=NH_2

Scheme 4

That rearrangement to the aryl acetates had not occurred with any of the compounds **11, 12, 14,** or **15** was convirmed by the presence of two *meta* coupled aromatic protons (J = *ca* 2 Hz) in the nmr spectra. In simpler systems [5] the rearrangements occur readily below 100°.

Possible mechanisms involve either a nitrenium ion **17** or a sigmatropic rearrangement **18** (Scheme 5).

17 18

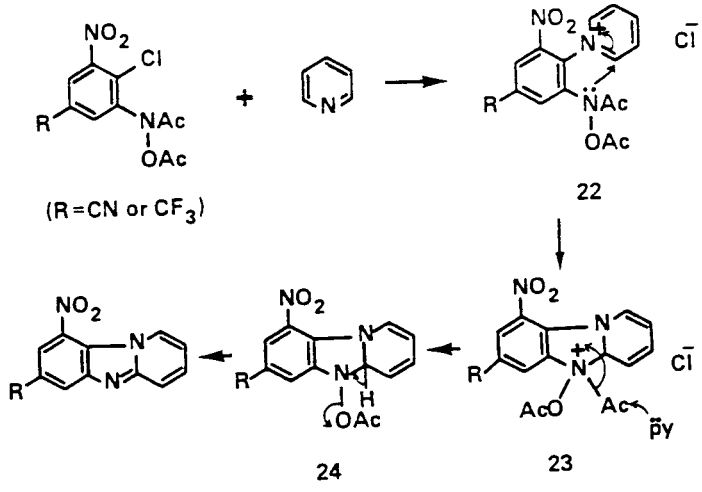
Scheme 5

Current knowledge [5] favors a nitrenium ion which may explain why a -OMe group accelerates [5] the reaction; whereas, in our case the -NO_2 and -CN groups greatly disfavor the reaction.

When attempts were made to acetylate the nitrohydroxylamine **6** with acetic anhydride-pyridine, only a small amount of the diacetyl compound **11** was formed. Instead, the major product **13** posssessed no acetyl groups and had incorporated pyridine. A much cleaner reaction was observed when **11** was stirred in pyridine at room temperature, under these conditions, **13** was the only product formed (Scheme 3). A similar sequence of reactions was observed for the trifluoromethyl compounds **19** → **20** → **21**. The identity of the final products **13** and **21** as pyrido[1,2-*a*]benzimidazoles was confirmed by an x-ray structure [6] of **21** [which formed better crystals than **13**].

Interestingly, this rearrangement with pyridine proceeded readily with the *mono-N*-acetylhydroxylamine **10**, but not with the free hydroxylamine **6** or the amino diacetylhydroxylamine **12**.

A possible mechanism for the transformation is shown in Scheme 6. It involves displacement of the chlorine by pyridine to give the pyridinium salt **22**.

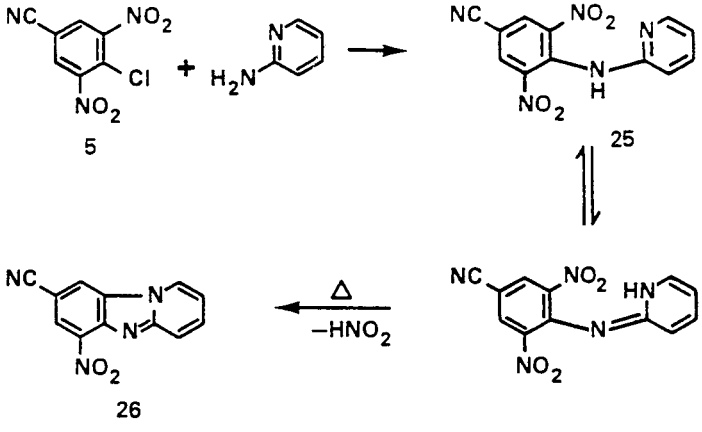


(R=CN or CF_3) 22 24 23

Scheme 6

The nitrogen of the hydroxylamine attacks the *ortho* position of the pyridine to form the tricyclic system **23**. Excess pyridine, or the counter ion chloride, removes the acetamide acetyl group to afford **24**, which simply loses acetic acid to give the pyrido[1,2-*a*]benzimidazole.

The pyrido[1,2-*a*]benzimidazole **26** that is isomeric with **13**, was prepared *via* the thermolysis [7] of the aminopyridine **25**, which in turn was prepared from **1** and 2-aminopyridine (Scheme 7).



5 25 26

Scheme 7

EXPERIMENTAL

4-Chloro-3-(hydroxyamino)-5-nitrobenzonitrile (**6**).

The dinitro compound **5** (Aldrich) (1.0 g, 4.4 mmoles) was dissolved in methanol (50 ml) and treated dropwise over 3 hours with a 20% aqueous solution (15 ml) of titanium trichloride. Triethylamine (2 ml) was added to the cooled reaction and the solvent removed *in vacuo*. Chloroform (10 ml) was added to the residue and a yellow solid was filtered. This material was the starting dinitro compound (0.33 g, 33%). The chloroform filtrate

was chromatographed over silica gel (100 g) at 10-15 psi, eluting with 3:1 chloroform:hexane to afford the nitrohydroxylamine **6** as fine yellow needles from methylene chloride: mp 140-143° dec (0.15 g, 16%); ir (Nujol): ν 3290, 3097, 2254, 1602, 1566, 1541, 1534, 1366, 1079, 1046, 926, 875, 864 cm^{-1}; nmr (D_6-DMSO): δ 7.58 (d, J = 2 Hz, H_2), 7.87 (d, J = 2 Hz, H_6), 9.36 (bd, NHOH); uv (methanol): λ max (ε) 222 (26,500), 338 (2,000); ms: (relative intensity) m/e 215 (33), 213 (100), 167 (38), 150 (29), 147 (19), 115 (32), 104 (29), 103 (54), 88 (31), 76 (24).

Anal. Calcd. for $C_7H_4ClN_3O_3$: C, 39.36; H, 1.89; N, 19.67; Cl, 16.60. Found: C, 39.23; H, 1.84; N, 19.80; Cl, 16.76.

4-Chloro-3,5-*bis*(hydroxyamino)benzonitrile (**7**).

The dinitro compound (**5**) (0.50 g, 2.2 mmoles) was dissolved in ethanol (25 ml) and 5% Pd/C catalyst (0.05 g) added. The mixture was hydrogenated at 5 psi for 15 minutes. The catalyst was filtered and the solvent removed to give a brown residue. The residue was chromatographed over silica gel (50 g) with a gradient elution of 1-10% methanol-methylene chloride. The dihydroxylamine **7** was obtained from the earlier fractions and recrystallized from methanol-methylene chloride (with a Darco treatment) as tan needles, mp 120° dec (0.1 g, 23%); ir (Nujol): ν 3400, 3260, 3200, 3100, 2240, 1685, 1580, 1500, 1485, 1420, 1395, 1380, 1325, 1030, 845, 785 cm^{-1}; uv (ethanol): λ max (ε) 211 (22,950), 234 (29,400), 270 (5,050), 324 (3,750); ms: (relative intensity) m/e 201 (54), 199 (100), 197 (81), 182 (69), 163 (55), 155 (95), 115 (49), 103 (73).

Anal. Calcd. for $C_7H_6ClN_3O_2$: C, 42.12; H, 3.03; N, 21.05; Cl, 17.77. Found: C, 42.07; H, 2.88; N, 22.46; Cl, 16.98 [8].

N-(Acetyloxy)-*N*-(2-chloro-5-cyano-3-nitrophenyl)acetamide (**11**).

The dinitro compound (**5**) (10.0 g, 44 mmoles) was dissolved in acetonitrile (200 ml) and 5% Pd/C catalyst (1.0 g) added. The mixture was hydrogenated at 8 psi for 50 minutes, then the catalyst filtered. The filtrate was treated dropwise with acetyl chloride (30 ml) and stirred for 4 hours. The solvent was removed to leave a brown solid, which was washed with methylene chloride (25 ml) to give a yellow solid. Recrystallization from acetone-hexane gave the product **11** as pale yellow crystals, mp 172-174° (6.65 g, 51%). Additional pure material (1.2 g, 9%) was obtained from the original methylene chloride wash and the filtrate of the above recrystallization, upon chromatography on silica gel (100 g) (methylene chloride); ir (Nujol): ν 3106, 3077, 2243, 1796, 1711, 1543, 1312, 1281, 1260, 1221, 1187, 1105, 1065, 1006, 919, 895, 876, 761, 753 cm^{-1}; nmr (D_6-DMSO): δ 2.17 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 8.43 (d, J = 2 Hz, H_6), 8.82 (d, J = 2 Hz, H_4); uv (methanol): λ max (ε) 223 (21,900), 300 (sh) (1,100); ms: (relative intensity) m/e 297 (1), 255 (2), 257 (7), 149 (9), 100 (8), 43 (100).

Anal. Calcd. for $C_{11}H_8ClN_3O_5$: C, 44.38; H, 2.71; N, 14.12; Cl, 11.91. Found: C, 44.65; H, 2.71; N, 14.25; Cl, 12.07.

N-(Acetyloxy)-*N*-(3-amino-2-chloro-5-cyanophenyl)acetamide (**12**).

The nitro diacetyl compound **11** (4.0 g, 13.44 mmoles) was dissolved in methanol (600 ml) upon warming, then allowed to cool to room temperature. A 20% aqueous solution of titanium trichloride (57 ml) was slowly added until a pink coloration remained. After 15 minutes triethylamine (40 ml) was added slowly to the cooled reaction. The mixture was taken to dryness *in vacuo* then water was added (500 ml). The aqueous mixture was extracted with chloroform (4 x 100 ml) and the organic solution dried, filtered and evaporated to give a tan solid. Recrystallization from acetone-hexane (with a Darco treatment) gave fine off-white needles, mp 138-140° dec (2.33 g, 65%); ir (Nujol): ν 3440, 3340, 3240, 2240, 1795, 1695, 1635, 1590, 1570, 1305, 1180, 1045, 1000, 865, 840 cm^{-1}; nmr (D_6-DMSO): δ 2.04 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 6.21 (s, 2H, NH_2), 7.11 (d, J = 2 Hz, H_4), 7.24 (d, J = 2 Hz, H_6); uv (ethanol): λ max (ε) 226 (28,850), 259 (7,100), 335 (4,550); ms: (relative intensity) m/e 269 (1), 267 (4), 227 (9), 225 (27), 185 (14), 183 (43), 167 (6), 139 (4), 138 (5), 57 (6), 43 (100).

Anal. Calcd. for $C_{11}H_{10}ClN_3O_3$: C, 50.32; H, 4.26; N, 14.43; Cl, 12.20. Found: C, 50.73; H, 4.31; N, 14.95; Cl, 12.55.

N-(2-Chloro-5-cyano-3-nitrophenyl-*N*-hydroxyacetamide (**10**).

The dinitro compound **5** (3.0 g, 13.2 mmoles) was dissolved in acetonitrile (75 ml) and 5% Pd/C catalyst (0.30 g) added. The mixture was hydrogenated for 20 minutes at 6 psi. The catalyst was filtered and the filtrate treated with acetyl chloride (5 ml) dropwise. After 2 hours the solvent was removed and the residue chromatographed over silica gel (250 g). Gradient elution with 0-4% methanol-methylene chloride afforded separation of the two products. The diacetyl compound **11** mp 171-173° (0.43 g, 11%) was eluted first followed by the monoacetyl hydroxylamine **10**. The latter was recrystallized from methylene chloride as yellow prisms, mp 155-156° (0.40 g, 12%); ir (Nujol): ν 3532, 3398, 3079, 2255, 1662, 1620, 1548, 1509, 1453, 1424, 1383, 1363, 1347, 1293, 1267, 1217, 1168, 1130, 1079, 1047, 1036, 977, 934, 925, 888, 843, 822, 757, 745, 722, 664 cm^{-1}; nmr (D_6-DMSO): δ 2.24 (s, 3H, CH_3), 8.40 (d, J = 1.5 Hz, H_6), 8.71 (d, J = 1.5 Hz, H_4), 11.18 (s, 1H, OH); uv (methanol): λ max (ε) 221 (25,700); ms: (relative intensity) m/e 257 (1), 255 (2), 213 (2), 197 (2), 194 (3), 149 (2), 100 (2), 98 (2), 88 (2), 44 (3), 43 (100).

Anal. Calcd. for $C_9H_6ClN_3O_4$: C, 42.29; H, 2.37; N, 16.44; Cl, 13.87. Found: C, 42.21; H, 2.60; N, 16.73; Cl, 13.73.

3-Amino-4-chloro-5-(hydroxyamino)benzonitrile (**8**).

The dinitro compound **5** (1.0 g, 4.4 mmoles) was dissolved in methanol (50 ml) and 5% Pd/C catalyst (0.1 g) added. The mixture was hydrogenated at 6 psi for 25 minutes, then the catalyst filtered. An aqueous solution (10 ml) of 20% titanium trichloride was added dropwise, while the reaction was monitored by tlc (5% methanol-chloroform) to prevent over reduction. Triethylamine (2 ml) was added to the cooled flask, then the solvent evaporated. Water (10 ml) was added to the residue and extracted with chloroform (2 x 75 ml). The chloroform extracts were chromatographed over silica gel (100 g) eluting with 2% methanol-chloroform. The aminohydroxylamine **8** was obtained as yellow plates from chloroform, mp 138° dec (0.147 g, 18%); ir (Nujol): ν 3406, 3293, 3203, 2226, 1585, 1044, 864, 783 cm^{-1}; nmr (D_6-DMSO): δ 5.60 (bd, s, 2H, NH_2), 6.58 (s, 2H, aromatic), 8.32 (bd, s, NH or OH), 8.58 (bd, OH or NH); uv (methanol): λ max (ε) 209 (22,500), 231 (31,800), 269 (sh) (3,650), 327 (3,700); ms: (relative intensity) m/e 185 (24), 183 (77), 169 (16), 168 (12), 167 (49), 166 (25), 148 (18), 141 (32), 139 (100), 103 (10).

Anal. Calcd. for $C_7H_6ClN_3O$: C, 45.79; H, 3.30; N, 22.89; Cl, 19.31. Found: C, 46.02; H, 3.27; N, 23.26; Cl, 19.81.

Thermolysis of the Aminodiacetylhydroxylamine (**12**).

The aminodiacetylhydroxylamine **12** (0.05 g, 0.19 mmoles) was heated under reflux in xylene (5 ml) for 24 hours. The solid which formed on cooling was collected and identified as the starting material (0.025 g, 50%). Tlc was rather complex, showing several slower moving components. The slowest component was isolated by chromatography (silica gel), 0.5% methanol-methylene chloride and identified as the acetamide **15**, mp 203-205°; ir (Nujol): ν 3404, 3310, 2230, 1683, 1580, 1545, 1261, 1058, 1050, 851 cm^{-1}; nmr (D_6-DMSO): δ 2.10 (s, 3H, CH_3), 5.85 (s, 2H, NH_2), 6.90 (d, J = 1.5 Hz, H_4), 7.32 (d, J = 1.5 Hz, H_6), 9.42 (s, NH); uv (methanol): λ max (ε) 234 (38,100), 260 (sh) (7,400), 328 (4,100); ms: (relative intensity) m/e 211 (10), 209 (30), 175 (10), 174 (8), 169 (4), 168 (12), 167 (100), 139 (9), 105 (11).

Anal. Calcd. for $C_9H_8ClN_3O$: C, 51.56; H, 3.84; N, 20.04; Cl, 16.92. Found: C, 52.06; H, 3.88; N, 19.80; Cl, 17.20.

Thermolysis of the Nitrodiacetylhydroxylamine **11**.

The nitrodiacetylhydroxylamine **11** (0.05 g, 0.17 mmoles) was heated under reflux in 1,2,4-trichlorobenzene (5 ml) for 24 hours. Tlc showed one major spot moving slower than the starting material. The solvent was removed and the residue chromatographed over silica gel (25 g) eluting with 3:1 chloroform:hexane. The suspected nitroacetamide **14** was obtained as tan prisms from methylene chloride-hexane, mp 190-193° (0.027 g, 67%); ms: (relative intensity) m/e 241 (2), 239 (14), 204 (9), 199 (32), 198 (9), 197 (98), 153 (8), 151 (27), 115 (23), 88 (12), 43 (100). A small portion of the nitroacetamide **14** was reduced with titanium trichloride to afford the aminoacetamide **15** identical in all respects with a sample

synthesized independently by acetylation of the diamine and from thermolysis of **12**.

9-Nitro-pyrido[1,2-*a*]benzimidazole-7-carbonitrile (**13**).

The nitrodiacetyl compound **11** (2.0 g, 6.7 mmoles) was dissolved in pyridine (10 ml) and stirred overnight at room temperature. The precipitate (1.1 g) was filtered and recrystallized from acetone as yellow needles, mp 275-277° dec (1.0 g, 63%); ir (Nujol): ν 3160, 3080, 2240, 1650, 1615, 1560, 1535, 1510, 1360, 1345, 1325, 920, 890, 785, 755, 750, 730 cm^{-1}; nmr (deuteriochloroform + D_6-DMSO): δ 7.20 (m, 1H), 7.75 (m, 2H), 8.35 (d, J = 1.5 Hz, 1H), 8.60 (d, J = 1.5 Hz, 1H), 8.80 (dt, J = 7.4 and 1.2 Hz, 1H); uv (methanol): λ max (ϵ) 237 (55,350), 268 (17,850), 340 (4,100), 378 (3,750); ms: (relative intensity) m/e 238 (96), 193 (16), 192 (100), 191 (15), 180 (16), 166 (12), 165 (43), 138 (10), 78 (13).

Anal. Calcd. for $C_{12}H_6N_4O_2$: C, 60.50; H, 2.54; N, 23.52. Found: C, 60.80; H, 2.54; N, 23.84.

N-(Acetyloxy)-*N*-[2-chloro-3-nitro-5-(trifluoromethyl)phenyl]acetamide (**20**).

4-Chloro-3,5-dinitrobenzotrifluoride (Aldrich) (5.0 g, 18.5 mmoles) was dissolved in acetonitrile (100 ml) and 5% Pd/C catalyst (0.5 g) added. The reaction was hydrogenated at 6 psi for 30 minutes, then the catalyst filtered. The filtrate was treated dropwise with acetyl chloride (15 ml) and stirred for 3 hours. Removal of the solvent gave a sticky residue which was chromatographed over silica gel (400 g) using a 0-1% methanol-methylene chloride gradient. The nitrohydroxylamine (diacetyl) **20** was eluted first and recrystallized from acetone-hexane as white crystals, mp 131-133° (1.48 g, 24%); ir (Nujol): ν 3098, 1802, 1710, 1621, 1549, 1238, 1208, 1180, 1140, 1129, 1109, 1090, 1062, 1050, 1034, 1007, 964, 921, 906, 899, 866, 764, 751 cm^{-1}; nmr (deuteriochloroform): δ 2.20 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 8.10 (m, 2H, aromatic); uv (ethanol): λ max (ϵ) 240 (sh) (5,300); ms: (relative intensity) m/e 343 (17), 342 (17), 341 (100), 285 (14), 283 (41).

Anal. Calcd. for $C_{11}H_8ClF_3N_2O_5$: C, 38.78; H, 2.37; N , 8.23; Cl, 10.41; F, 16.73. Found: C, 38.89; H, 2.33; N, 8.36; Cl, 10.30; F, 16.88.

9-Nitro-7-(trifluoromethyl)pyrido[1,2-*a*]benzimidazole (**21**).

The diacetyl compound (**20**) (0.50 g, 1.47 mmoles) was stirred overnight in pyridine (1 ml) and the resultant precipitate filtered. The solid was chromatographed over silica gel (30 g) eluting with chloroform. Recrystallization of the product from acetone-hexane gave fine bright yellow needles; mp 158-159.5° (0.21 g, 51%); ir (Nujol): ν 1649, 1538, 1529, 1506, 1271, 1247, 1239, 1198, 1161, 1144, 1137, 1098, 1091, 1022, 1003, 903, 899, 888, 873, 833, 815, 782, 760, 753, 740, 735, 667 cm^{-1}; nmr (deuteriochloroform): δ 7.00 (m, 1H), 7.67 (m, 2H), 8.30 (s, 1H), 8.48 (s, 1H), 9.02 (dd, J = 1 and 7.5 Hz, 1H); uv (ethanol): λ max (ϵ) 213 (27,200), 233 (47,350), 263 (14,500), 327 (3,850), 376 (3,550); ms: (relative intensity) m/e 282 (10), 281 (65), 262 (7), 236 (14), 235 (100), 223 (13), 215 (7), 166 (9), 78 (16), 51 (7).

Anal. Calcd. for $C_{12}H_6F_3N_3O_2$: C, 51.25; H, 2.15; N, 14.94; F, 20.27. Found: C, 51.53; H, 2.08; N, 15.29; F, 19.84.

3,5-Dinitro-4-(2-pyridinylamino)benzonitrile (**25**).

The dinitro compound **5** (0.5 g, 2.2 mmoles) was dissolved in acetonitrile (10 ml) and 2-aminopyridine (0.25 g, 2.6 mmoles) added. After stirring overnight, additional 2-aminopyridine (0.30 g, 3.2 mmoles) was added. After 1 hour the solvent was removed and the residue crystallized from acetone to give brick red prisms, mp 170-174° dec (0.15 g, 24%). The filtrate was chromatographed over silica gel (50 g) eluting with methylene chloride to afford more product, mp 182-184° dec (0.26 g, 41%) from acetone; ir (Nujol): ν 3354, 3088, 2238, 1623, 1601, 1539, 1452, 1277, 920, 775 cm^{-1}; nmr (D_6-DMSO): δ 6.97 (m, 1H), 7.18 (d, J = 8 Hz, 1H), 7.74 (m, 1H), 7.97 (dd, J = 1.5 and 5.5 Hz, 1H), 8.76 (m, 2H), 10.18 (bd, NH); uv (methanol): λ max (ϵ) 221 (21,950), 239 (sh) (17,800), 276 (16,700), 368 (8,000); ms: (relative intensity) m/e 285 (6), 240 (14), 239 (96), 209 (10), 194 (17), 193 (100), 192 (36), 165 (13), 79 (10), 78 (40).

Anal. Calcd. for $C_{12}H_7N_5O_4$: C, 50.53; H, 2.47; N, 24.56. Found: C, 50.48; H, 2.55; N, 24.87.

6-Nitropyrido[1,2-*a*]benzimidazole-8-carbonitrile (**26**).

The aminopyridine derivative **25** (0.43 g, 1.51 mmoles) was heated under reflux in xylene (20 ml) for 18 hours. Upon cooling a jade green solid separated. This solid was recrystallized from acetone (with a Darco treatment) as bright yellow prisms, mp 322-323° dec (0.28 g, 78%); ir (Nujol): ν 3115, 3099, 3079, 3059, 3030, 2229, 1620, 1568, 1521, 1489, 1361, 1354, 1327, 1287, 1264, 1249, 1141, 895, 857, 775, 766, 620, 614 cm^{-1}; nmr (D_6-DMSO): 7.33 (m, 1H), 7.92 (m, 2H), 8.70 (m, 1H), 9.26 (m, 2H); uv (ethanol): λ max (ϵ) 219 (29,750), 226 (28,700), 240 (24,750), 247 (25,100), 267 (29,900), 305 (sh) (3,200), 398 (10,050); ms: (relative intensity) m/e 239 (15), 238 (100), 208 (27), 193 (9), 192 (59), 191 (12), 180 (12), 166 (8), 165 (28), 78 (10).

Anal. Calcd. for $C_{12}H_6N_4O_2$: C, 60.50; H, 2.54; N, 23.52. Found: C, 60.45; H, 2.64; N, 23.68.

Acknowledgements.

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