Carbon-Nitrogen Bond Formation in Cyclisation by Deoxygenation, Thermolysis or Photolysis of Phenylimidazo[1,2-*a*][1,8]naphthyridines

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Triethyl phosphite deoxygenation of 2-(2-nitrophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**3**) led to the *C*-insertion to give the indoloimidazonaphthyridine **5**. Our attempt to promote the *N*-insertion by blocking the C-3 position failed. Triethyl phosphite deoxygenation of 1-nitroso-2-(4-fluorophenyl)imidazo[1,2-*a*][1,8]-naphthyridine (**12**) led to the corresponding amine structure (**15**). Thermolysis and photolysis of 6,8-dimethyl-2-(2-azidophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**17**) are also reported.

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Introduction.

Deoxygenation of *C*-nitroso (or nitro) derivatives by triethyl phosphite is known to give reductive cyclisation to a variety of heterocyclic systems presumably *via* a nitrene when an excess of reducing agent is used [1].

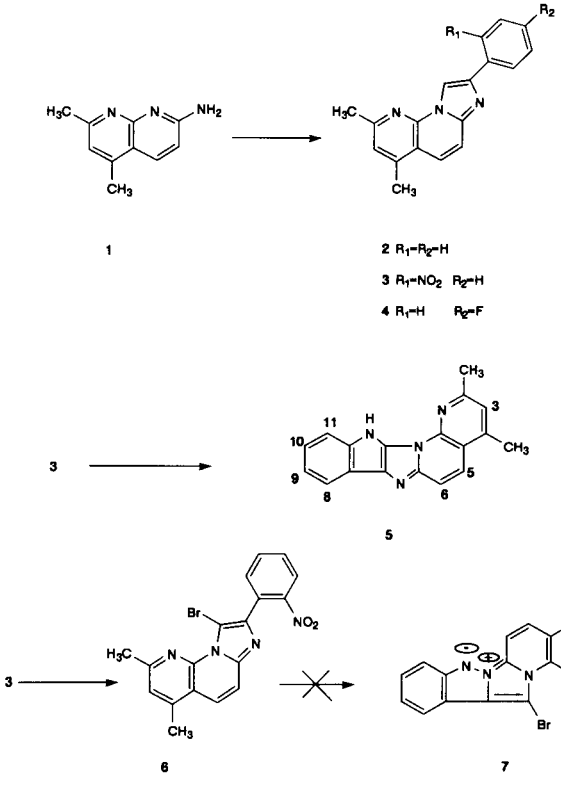
Recently we have reported that the reaction of 2-*o*-nitrophenylimidazo[1,2-*a*]pyridine with triethyl phosphite gives the indole system by heterocyclisation [2].

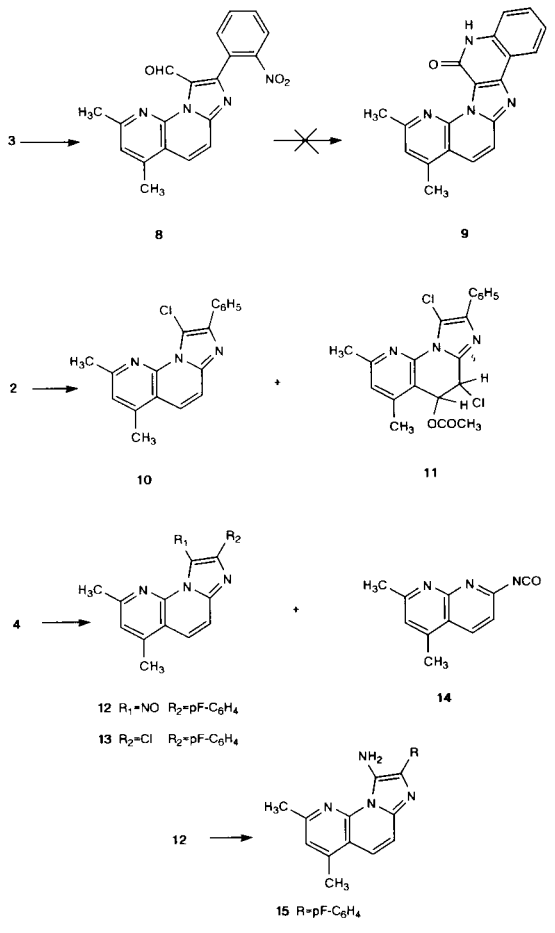
In continuation of our studies on the reactivity of nitrogen bridgehead azaindolizines, we have now investigated the reactivity of 2-(2-nitrophenyl) or (2-azidophenyl)imidazo[1,2-*a*][1,8]naphthyridines.

Results and Discussion.

Condensation of 2-amino-5,7-dimethyl[1,8]naphthyridine (**1**) with appropriate bromacetophenones gave the corresponding imidazo[1,2-*a*][1,8]naphthyridines **2-4**.

Deoxygenation of 6,8-dimethyl-2-(2-nitrophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**3**) with hot triethyl phosphite led to *C*-insertion rather than *N*-insertion to give 2,4-dimethylindolo[3',2':4,5]imidazo[1,2-*a*][1,8]naphthyridine (**5**) with a 28% yield. Structural determination of **5** was made on the basis of ^{1}H nmr and mass spectroscopy. Proton assignment was made by comparison with results obtained





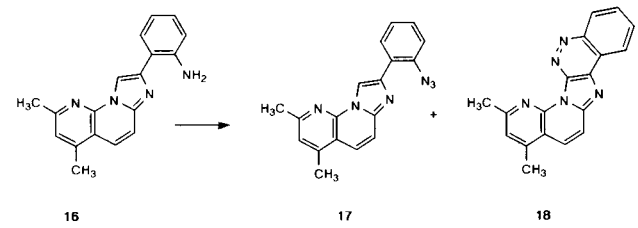
in the imidazo[1,2-*a*]pyridine series [3], and gave the following values: H(3) (7.38) - H(5,6) (AB system, 7.65) - H(8) (7.76) - H(9) (7.32) - H(10) (7.23) - H(11) (7.91). The ^{13}C nmr spectrum, in accord with the proposed structure, revealed the presence of seven aromatic CH, nine quaternary carbons and two methyl signals. Examination of the mass spectrum gave its molecular weight at m/z: 286.

In order to obtain *N*-insertion, we decided to block the 1-position by bromination of **3**. Our attempts to give the desired heterocycle **7** were unproductive, only tars were obtained. From this result, we investigated the possibility of promoting insertion on a carbonyl function. Recently, Ollis *et al* reported the participation of such a formyl group in the triethyl phosphite deoxygenation of 3-formyl-2-(2-nitrophenyl)imidazo[1,2-*a*]pyridine [4]. In our case, the reaction of the formyl derivative **8** obtained by Vilsmeier-Haack reaction on **3**, with hot triethyl phosphite did not give to the structure **9**. Then we investigated the synthesis of pentacyclic structure **5** by reductive cyclisation of nitroso derivatives. Nitrosation of **2** with sodium nitrite in acetic acid media failed. Treatment by nitrosyl chloride in acetic acid did not give the desired nitroso compound but the chloro derivative **10** admixed with an addition product **11**. Treated in the same media, compound **4** gave rise to a mixture of nitroso compound **12**, chloro derivative **13** and naphthyridine **14**. The molecular formula of compound **11** was established as $C_{20}H_{17}O_2N_3Cl_2$ by hight-resolution mass spectrometry. The ^1H nmr spectrum revealed the presence of six aromatic protons, two aliphatic protons and three methyl groups. Considering the above result and the chemical shifts (δ_C 169.72, 114.0) of a carbonyl group and C(1) demonstrated by technic of parity determination by coupling constant modulation with composite pulses and quantitative ^{13}C nmr experiments, thus this compound was substituted at the C(1)-position with addition on the C(4)/C(5) bond. The shifts of the quaternary carbons C(1), C(4) and C(5) at δ_C 114.0, 48.6 and 67.5 respectively were in accord with the proposed structure. The *cis* relation between the $OCOCH_3$ and Cl groups was determinated by difference nuclear Overhauser effect (DNOE) experiments. Irradiation of the signal for the methyl signal at C(6) (δ_H 2.45) brought about enhancement of the H(7) (δ_H 7.02, 12%) and H(5) (δ_H 6.32, 20%) signals. When the H(4) signal (δ_H 5.39) was irradiated, a strong enhancement of the H(5) signal (δ_H 6.32, 16%) was observed. Considering that irradiation of the signal for the H(5) (δ_H 6.32) caused enhancement of the signals of the 6-methyl (δ_H 2.45, 6%), $OCOCH_3$ group (δ_H 2.03, 2%) and H(4) and H(5) was 3 Hz, the H(4)(5) must be in a *cis* position.

In mass spectrometry, compounds **10** and **13** showed m/z 307-309 and 323-327 (100-33% respectively). Comparison of the δ_H chemical shifts of **10, 12** and **13** with **2** led to the required information on the substitution, considered to be located at the C(1) position. Assignments by usual criteria of ir, ^1H and ^{13}C nmr spectroscopy agreed with the isocyanonaphthyridine structure **14**. Interestingly, the ir spectrum showed the presence of a signal at ν max 2260 cm^{-1} typical of a NCO group. The ^{13}C nmr assignments obtained from JMPC and quantitative experiments confirmed this structure with, in particular the presence of two quaternary carbons at δ_C 160.1 corresponding to C(2) and C(7), the carbon of the isocyanate group resonate at high field (δ_C 104.4).

Deoxygenation of **12** with triethyl phosphite at low temperature (45°) led to the amine **15**.

We then investigated photolysis and thermolysis of azidophenyl compounds. Reduction of **3** with hydrochloric acid/tin gave the corresponding amine **16** and this on



treatment with sodium nitrite/hydrochloric acid/sodium azide at 0° for one hour gave the expected azide **17** admixed with the cinnoline **18** in 52 and 6% yield, respectively. The structure of **17** was detemined by a ν max 2180 cm^{-1} characteristic of the azido band. Confirmation of structural assignments was made by mass spectrometry with a m/z: 314 and 286 (100%). The ^1H nmr spectrum of the cinnoline **18** revealed characteristic ABXY system [2] with the following values: H(3) (7.15) - H(5) (7.69) - H(6) (7.99) - H(8) (8.69) - H(9) (7.89) - H(10) (7.89) - H(11) (8.75). This structure was confirmed by mass spectrometry with a m/z 299 (M^+) and 271 (M^+-N_2) [6].

Both thermolysis in 1,2,4-trichlorobenzene and photolysis in methylene chloride of **17** led to compound **5** in 35% and 12% yield respectively. When cyclisation is carried out in boiling 6*N* hydrochloric acid [7], the azide **17** is stable and no *C*-insertion is observed.

EXPERIMENTAL

General Details.

Melting points were determined on a Büchi capillary apparatus and are not corrected. Elemental analyses were performed by Microanalytical Center, ENSCM, Montpellier. The ^1H nmr spectra were recorded with Varian EM 360 (60 MHz) or Brüker WM 90 or a Brüker MSL 300; ^{13}C chemical shifts are reported in ppm from TMS with the centre resonance of deuteriochloroform as an internal reference for ^{13}C (77.10 ppm) and with the small amount of residual chloroform as an internal reference from the ^1H spectrum (7.27 ppm). The ir spectra were obtained on a Beckman AccuLab 2 spectrometer. Mass spectra were recorded on a LKB 2091 spectrometer at 70 eV [(θ_{source}) = 180°]. Compounds were purified by high-performance liquid chromatography (hplc), Waters M 590 on a preparative alumina column. When necessary, solvents and reagents were dried prior to use. Methylene chloride was dried over activated alumina and distilled from calcium hydride. Thin layer chromatography (tlc) were performed on 0.25 mm E. Merck precoated neutral alumina plates. The photolysis solution was irradiated internally using a 100 W medium-pressure mercury lamp (Hanovia) with a Pyrex filter.

General Procedure for Preparation of Compounds **2-4**.

To a solution of 2-amino-5,7-dimethyl[1,8]naphthyridine (**1**) (10 g, 57.8 mmoles) in ethanol (20 ml) was added the appropriate bromoacetophenone (75 mmoles). The mixture was stirred and refluxed for 3 hours. After cooling, the solution was evaporated, poured into water (200 ml) and basified with sodium carbonate. Aqueous layers were extracted with methylene chloride, dried and evaporated *in vacuo*. The residual oil was submitted to chromatography on neutral alumina eluted with methylene chloride.

6,8-Dimethyl-2-phenylimidazo[1,2-*a*][1,8]naphthyridine (**2**).

This compound was obtained with a 34% yield as yellow prisms, mp 175-177°; ^1H nmr (deuteriochloroform): 300 MHz, δ 2.48 (s, 8-CH_3), 2.62 (s, 6-CH_3), 6.95 (s, H-7), 7.37 (m, H-4'), 7.43 (m, H-3', 5'), 7.48 (m, H-4, 5), 8.05 (d, H-2', 6'), 8.62 (s, H-1); ^{13}C nmr (deuteriochloroform): 75 MHz, δ 18.51 (6-CH_3), 24.57 (8-CH_3), 107.48 (C-1), 114.51 (C-5a), 115.97 (C-4), 120.81 (C-5), 122.07 (C-7), 125.77 (C-2', 6'), 127.59 (C-4'), 128.62 (C-3', 5'), 133.91 (C-2), 142.61 (C-1'), 144.35 (C-3a), 144.70 (C-9a), 146.07 (C-6), 157.92 (C-8).

Anal. Calcd. for $C_{18}H_{15}N_3$: C, 79.12; H, 5.49; N, 15.38. Found: C, 79.0; H, 5.3; N, 15.5.

6,8-Dimethyl-2-(2-nitrophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**3**).

This compound was obtained with a 30% yield as yellow prisms, mp 212-214°; ^1H nmr (deuteriochloroform): 300 MHz, δ 2.61 (s, 6-CH_3), 2.67 (s, 8-CH_3), 7.12 (s, H-7), 7.47 (m, H-4'), 7.56 (m, H4, 5), 7.62 (m, H-5'), 7.73 (d, H-6'), 7.99 (d, H-3'), 8.65 (s, H-1); ^{13}C nmr (deuteriochloroform): 75 MHz, δ 18.71, 24.73, 110.23, 114.83, 116.41, 121.67, 122.65, 123.74, 128.04, 128.3, 131.22, 131.66, 139.40, 142.91, 144.77, 146.39, 149.22, 158.43.

Anal. Calcd. for $C_{18}H_{14}N_4O_2$: C, 67.92; H, 4.40; N, 17.61. Found: C, 67.7; H, 4.3; N, 17.8.

6,8-Dimethyl-2-(4-fluorophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**4**).

This compound was obtained with a 43% yield as white prisms, mp 201-203°; ^1H nmr (deuteriochloroform): 60 MHz, δ 2.60 (s, 6-CH_3), 2.68 (s, 8-CH_3), 7.11 (d, H-2', 6'), 7.15 (s, H-7), 7.56 (m, H-4, 5), 7.99 (d, H-3', 5'), 8.64 (s, H-1).

Anal. Calcd. for $C_{18}H_{14}N_3F$: C, 74.23; H, 4.81; N, 14.43. Found: C, 74.3; H, 4.6; N, 14.5.

2,4-Dimethylindolo[3',2':4,5]imidazo[1,2-*a*][1,8]naphthyridine (**5**).

To a freshly distilled triethyl phosphite (10 ml, 50 mmoles) was added **3** (2 g, 6.3 mmoles). The stirred mixture was refluxed for 4 hours under nitrogen, then cooled to room temperature. The mixture was treated with ether and the solid which precipited was filtered and chromatographed on silica gel. Elution with methylene chloride gave **5** (500 mg, 28%) as yellow prisms, mp >300°; ^1H nmr (dimethyl sulfoxide-d_6): 300 MHz, δ 2.70 (s, 4-CH_3), 2.81 (s, 2-CH_3), 7.23 (t, H-10), 7.32 (t, H-9), 7.38 (s, H-3), 7.65 (AB system, H-5, 6), 7.76 (d, H-8), 7.91 (d, H-11), 11.80 (s, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): 75 MHz, δ 17.82, 23.74, 112.94, 113.73, 116.65, 117.50, 117.70, 118.61, 119.21, 121.34, 121.91, 129.00, 130.90, 140.10, 142.32, 142.75, 145.62, 156.81; ms: (EI) 286 (M^+, 100%), 157 (36), 143 (11).

Anal. Calcd. for $C_{18}H_{14}N_4$: C, 75.52; H, 4.89; N, 19.58. Found: C, 75.3; H, 4.9; N, 19.6.

Thermal Decomposition of the Azide **17**.

A solution of the azide **17** (300 mg, 0.95 mmole) in anhydrous 1,2,4-trichlorobenzene (1 ml) was added dropwise over 1 minute to vigorously stirred 1,2,4-trichlorobenzene (5 ml) under dry nitrogen at 185°. When no azide could be detected (ir), the solvent was evaporated and the residue was chromatographed on silica gel with methylene chloride as eluent to afford **5** in 35% yield.

Photolysis of the Azide **17**.

Using the apparatus described at the beginning of the Experimental, with water cooling for an ambient temperature reaction, pure nitrogen was passed through the solution of **17** (0.2 g) in methylene chloride (200 ml). The reaction was monitored by following the disappearance of the azide ir, absorption (1 hour). After removal of the solvent, the residue was chromatographed as above to give **5** in 12% yield.

1-Bromo-6,8-dimethyl-2-(2-nitrophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**6**).

To a solultion of **3** (5 g, 15.7 mmoles) in acetic acid (100 ml) at 30° was added dropwise 1.6 ml of bromine (5.1 g, 31.8 mmoles). The mixture was stirred at room temperature for 10 minutes and filtered. The precipitate was suspended in water, made basic with sodium carbonate and extracted with methylene chloride. The filtrate was evaporated to give after ion chromatography (silica gel-methylene chloride) 3.5 g of **6** (56%), mp 244-246°; ^{1}H nmr (deuteriochloroform): 60 MHz, δ 2.67 (s, 6-CH_3), 2.72 (s, 8-CH_3), 7.23 (s, H-7), 7.64 (s, H-4, 5), 7.83 (s, H-4', 5', 6'), 8.15 (m, H-3').

Anal. Calcd. for $C_{18}H_{13}BrN_4O_2$: C, 54.40; H, 3.27; N, 14.10. Found: C, 54.2; H, 3.2; N, 14.2.

1-Formyl-6,8-dimethyl-2-(2-nitrophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**8**).

Phosphoryl chloride (0.9 ml) was added with stirring to a cooled *N,N*-dimethylformamide (4 ml). Compound **3** was then added portionwise. The mixture was stirred at room temperature for 30 minutes and heated at 104° for one hour. After being cooled, water was added. The formed precipitate was collected and chromatographed on silica gel (eluent: methylene chloride-methyl alcohol 95:5 v/v) to give 1.2 g (55%) of **8**, mp >300°; ^{1}H nmr (deuteriochloroform): 300 MHz, δ 2.70 (s, 6-CH_3), 2.74 (s, 8-CH_3), 7.26 (s, H-7), 7.61 (m, H-4'), 7.69 (m, H-3', 5'), 7.80 (AB system, H-4, 5), 8.15 (d, H-3'), 11.52 (s, CHO).

Anal. Calcd. for $C_{19}H_{14}N_4O_3$: C, 65.89; H, 4.05; N, 16.18. Found: C, 66.0; H, 3.9; N, 16.0.

1-Chloro-6,8-dimethyl-2-phenylimidazo[1,2-*a*][1,8]naphthyridine (**10**) and 5-Acetoxy-1,4-dichloro-6,8-dimethyl-2-phenyl-4,5-dihydroimidazo[1,2-*a*][1,8]naphthyridine (**11**).

To a cooled solution (0°) of acetic anhydride/acetic acid/potassium acetate (20 ml/10 ml/1 g) and 2 g (7.3 mmoles) of **2** was added 4.5 ml of nitrosyl chloride (0.37 g/ml) in acetic anhydride. After stirring at room temperature for 10 minutes, the mixture was added to crushed ice and filtered. The precipitate was chromatographed on silica gel and eluted with methylene chloride to give **11** (644 mg, 22%), mp 142-144°; ^{1}H nmr (deuteriochloroform): 300 MHz δ 2.03 (s, $OCOCH_3$), 2.45 (s, 6-CH_3), 2.60 (s, 8-CH_3), 5.39 (d, J = 3 Hz, H-4), 6.32 (d, H-5), 7.02 (s, H-7), 7.36 (t, J = 8 Hz, H-4'), 7.46 (t, J = 8 Hz, H-3', 5'), 8.03 (d, J = 8 Hz, H-2', 6'); ^{13}C nmr (deuteriochloroform): 75 MHz, δ 18.76 (6-CH_3), 20.82 ($OCOCH_3$), 24.07 (8-CH_3), 48.51 (C-4), 67.58 (C-5), 113.72 (C-1), 114.10 (C-5a), 123.63 (C-7), 127.15 (C-2', 6'), 127.91 (C-4'), 128.45 (C-3', 5'), 131.97 (C-2), 138.33 (C-1'), 141.10 (C-3a), 146.68 (C-9a), 149.62 (C-6), 158.75 (C-8), 169.71 (CO); ms: (EI) 405 (M + 4, 11%), 403 (M + 2, 1.86), 401 (M^+, 2.81), 343 (10.21), 341 (15.6), 324 (3.6), 85 (11.3), 83 (100).

Anal. Calcd. for $C_{20}H_{17}Cl_2N_3O_2$: C, 59.70; H, 4.23; N, 10.45. Found: C, 59.5; H, 4.3; N, 10.4.

Further elution gave the 1-chloro derivative **10** (1.37 g, 61%), mp 150-152°; ^{1}H nmr (deuteriochloroform): 300 MHz δ 2.58 (s, 6-CH_3), 2.68 (s, 8-CH_3), 7.11 (s, H-7), 7.39 (t, H-4'), 7.50 (m, H-4, 5, 3', 5'), 8.15 (d, H-2', 6'); ^{13}C nmr (deuteriochloroform): 75 MHz, δ 19.10 (CH_3), 24.64 (CH_3), 110.67 (C-1), 115.59 (C-5a), 116.54 (C-4), 121.59 (C-5), 122.45 (C-7), 128.03 (C-3', 5'), 128.44 (C-2', 6'), 132.87 (C-2), 140.29 (C-1'), 143.65 (C-3a), 144.99 (C-9a), 145.72 (C-6), 156.93 (C-8); ms: (EI) 309 (M + 2, 55%), 307 (M^+, 100).

Anal. Calcd. for $C_{18}H_{14}ClN_3$: C, 70.24; H, 4.55; N, 13.66. Found: C, 70.0; H, 4.6; N, 13.7.

6,8-Dimethyl-1-nitroso-2(4-fluorophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**12**), 1-Chloro-6,8-dimethyl-2-(4-fluorophenyl) imidazo-[1,2-*a*][1,8]naphthyridine (**13**) and 2-Isocyano-5,7-dimethyl[1,8]-naphthyridine (**14**).

These compounds were prepared using the above procedure employed for **10**. A chromatography on silica gel (eluent:methylene chloride) gave successively (**14**) (7%), mp 256-258°; ir (potassium bromide): 2260 (NCO) cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): 300 MHz δ 2.53 (s, 6, 8-CH_3), 6.67 (d, H-3), 7.26 (s, H-6), 8.19 (d, H-4); ^{13}C nmr (dimethyl sulfoxide-d_6): 75 MHz, δ 17.54 (6-CH_3), 23.88 (8-CH_3), 104.41 (Al-CO), 112.11 (C-4a), 118.67 (C-3), 122.98 (C-6), 138.45 (C-4), 147.03 (C-8a), 148.21 (C-5), 160.12 (C-2, 7); ms: (EI) 199 (M^+, 100%), 171 (67), 156 (26), 144 (19).

Anal. Calcd. for $C_{11}H_9N_3O$: C, 66.33; H, 4.52; N, 21.11. Found: C, 66.1; H, 4.4; N, 21.2.

Further elution gave **13** (180 mg, 7%), mp 202-204°; ^{1}H nmr (deuteriochloroform): 60 MHz, δ 2.63 (s, 6-CH_3), 2.70 (8-CH_3), 7.30 (m, H-7, 2', 6'), 7.60 (d, H-4, 5), 8.16 (m, H-3', 5'); ms: (EI) 327 (M + 2, 37%), 325 (M^+, 100).

Anal. Calcd. for $C_{18}H_{13}ClFN_3$: C, 66.36; H,, 3.99; N, 12.90. Found: C, 66.5; H, 4.0; N, 12.7.

The final elution gave **12** (40 mg, 2%), mp 192-194°; ^{1}H nmr (deuteriochloroform): 60 MHz, δ 2.76 (s, 6, 8-CH_3), 7.22 (m, H-2', 6'), 7.32 (s, H-7), 7.63 (d, H-4), 8.11 (d, H-5), 8.38 (m, H-3', 5').

Anal. Calcd., for $C_{18}H_{13}FN_4O$: C, 67.50; H, 4.06; N, 17.50. Found: C, 67.7; H, 4.0; N, 17.3.

1-Amino-6,8-dimethyl-2-(4-fluorophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**15**).

To a freshly distilled triethyl phosphite (3 ml) was added **12** (100 mg, 0.3 mmole). The solution was stirred for 15 minutes at 45°. After cooling the mixture was chromatographed (silica gel/ether) to give the amine **15** (40 mg, 43%), mp 216-218°; ^{1}H nmr (deuteriochloroform): 60 MHz, δ 2.60 (s, CH_3), 2.64 (s, CH_3), 6.20 (s, NH_2), 7.08 (m, H-2', 6'), 7.11 (s, H-7), 7.36 (s, H-4, 5), 8.00 (m, H-3', 5'); ms: (EI) 306 (M^+, 100%), 158 (91).

Anal. Calcd. for $C_{18}H_{15}FN_4$: C, 70.59; H, 4.90; N, 18.30. Found: C, 70.7; H, 4.7; N, 18.2.

6,8-Dimethyl-2-(2-aminophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**16**).

To a suspension of tin (2 g) in hydrochloric acid (20 ml) at −8° was added portionwise 2 g (6.3 mmoles) of the nitro derivative **3**. The solution was stirred for 2 hours, basified with sodium carbonate, extracted three times with chloroform and dried to give 1.7 g (93%) of **16** as pale yellow plates, mp 190-192°; ^{1}H nmr (deuteriochloroform): 60 MHz, δ 2.57 (s, CH_3), 2.60 (s, CH_3), 4.25 (s, NH_2), 6.80 (m, H-5', 6'), 7.1 (s, H-7), 7.10 (m, H-4'), 7.55 (s, H-4, 5), 7.70 (m, H-3'), 8.70 (s, H-1); ms: (EI) 288 (M^+, 100%), 157 (30).

Anal. Calcd. for $C_{18}H_{16}N_4$: C, 75.00; H, 5.56; N, 19.44. Found: C, 74.8; H, 5.6; N, 19.

6,8-Dimethyl-2-(2-azidophenyl)imidazo[1,2-*a*][1,8]naphthyridine (**17**) and 2,4-Dimethyl[1,8]naphthyridino[1',2':1,2]imidazo[5,4-*c*]-cinnoline (**18**).

A cooled solution of amine **16** (1.5 g, 5.2 mmoles) in hydrochloric acid/water (2.4/7.8 ml) was treated by sodium nitrite in water (800 mg/2 ml). The mixture was stirred for 10 minutes and added to a solution of sodium azide (800 mg), sodium acetate (5.1 g) in water (25 ml). After being stirred for 3 hours at 25°, the mixture was made basic (sodium carbonate), extracted with methylene

chloride, dried (sodium sulfate) and concentrated *in vacuo*. Chromatography on silica gel eluted with ether gave the expected azide **17** (470 mg, 52%), mp 192-194°; ir (potassium bromide): 2120 (N_3) cm^{-1}; ^1H nmr (deuteriochloroform): 300 MHz, δ 2.62 (s, 6-CH_3), 2.72 (s, 8-CH_3), 7.09 (s, H-7), 7.30 (m, H-4', 5', 6'), 7.55 (AB system, H-4, 5), 8.35 (d, H-3'), 9.05 (s, H-1); ^{13}C nmr (deuteriochloroform): 75 MHz, δ 16.78 (CH_3), 24.62 (CH_3), 111.77, 114.82, 116.17, 116.70, 121.29, 122.37, 125.10, 125.52, 128.54, 129.58, 136.52, 139.75, 143.10, 144.04, 146.27, 158.31; ms: (EI) 314 (M^+, 1%), 286 (100), 157 (33).

Anal. Calcd. for $C_{18}H_{14}N_6$: C, 68.79; H, 4.66; N, 26.75. Found: C, 68.9; H, 4.5; N, 26.5.

Further elution with methylene chloride gave the 2,4-dimethyl-[1,8]naphthyridino[1',2':1,2]imidazo[5,4-*c*]cinnoline **18** (110 mg, 6%), mp >300°; ^1H nmr (deuteriochloroform): 300 MHz, δ 2.60 (s, CH_3), 2.90 (s, CH_3), 7.15 (s, H-3), 7.69 (d, H-5), 7.89 (m, H-9, 10), 7.99 (d, H-6), 8.69 (m, H-8), 8.75 (m, H-11); ^{13}C nmr (deuteriochloroform): 75 MHz, δ 19.87 (CH_3), 25.27 (CH_3), 115.34 (C-4a), 116.26 (C-6), 119.76 (C-13a), 121.87 (C-5), 123.08 (C-3), 129.06 (C-9, C-10), 130.56 (C-8), 130.88 (C-11), 133.66 (C-7a), 145.09, 145.50, 146.38, 147.78, 149.73 for C-4, C-14a, C-6a, C-7b, C-11a, 161.19 (C-2); ms: (EI) 299 (M^+, 100%), 271 (M^+-N_2) (29), 255 (10).

Anal. Calcd. for $C_{18}H_{13}N_5$: C, 72.24; H, 4.35; N, 23.41. Found: C, 71.9; H, 4.4; N, 23.5.

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