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Reinvestigation of Rearrangement of Benzodiazepinediones into Quinoleines Under Microwave or Conventional Heating Conditions

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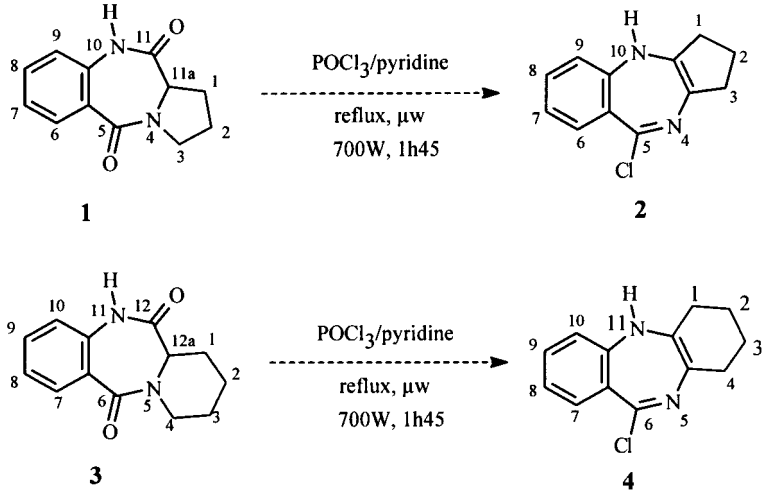
Abstract—Microwave or conventional heating of pyrrolo and pyrido[2,1-*c*][1,4]benzodiazepines in boiling phosphorus oxychloride led to rearranged products like benzo[*h*][1,6]naphthyridine and azepino[3,2-*c*]quinoleine and not to cyclopenta[*b*][1,4]benzodiazepine and tetrahydrodibenzo[*b*,*f*][1,4]diazepine as initially described.

Introduction

In a preliminary communication we described[1] that rearrangement of 1,2,3,10,11,11a-hexahydro-5*H*-pyrrolo[2,1-*c*][1,4]-benzodiazepine-5,11-dione **1** and 1,2,3,4,6,11,12,12a-octahydro-pyrido[2,1-*c*][1,4]benzodiazepine-6,12-dione **3**[2,3], respectively into 5-chloro-1,2,3,10-tetrahydro-cyclopenta-[*b*][1,4]benzodiazepine **2** and 6-chloro-1,2,3,4-tetrahydro-11*H*-dibenzo[*b*,*f*][1,4]diazepine **4**, occurred under drastic conditions with boiling phosphorus oxychloride and a catalytic amount of pyridine, only when these reactions were carried out under microwave heating conditions (Scheme 1). In a second communication[4], we demonstrated that similar rearrangements could be produced with or without microwave heating conditions. That's why we have reinvestigated the experimental conditions of this rearrangement in great detail adjusting several parameters (quantity of starting material, volume of $POCl_3$, catalytic amount of pyridine, temperature, heating conditions and reaction time).

The more representative results are summarized in Table 1. They clearly indicate that rearrangement can occur in



1 **2** **3** **4**

Scheme 1.

Keywords: benzodiazepines; quinoleins; naphthyridine; rearrangement.

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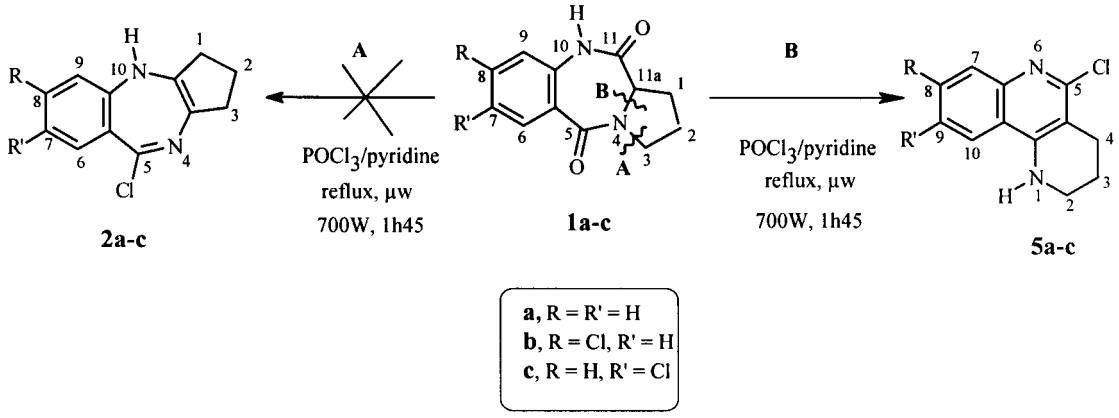
Table 1. Experimental conditions (comparison between conventional or microwave heating with or without pyridine)

Starting material (**1a**)	$POCl_3$/ pyridine	Temperature (°C)	Heating conditions	Time	Relative % rearranged product [a]	Relative % starting material [a]	Global yield isolated rearranged product (**5a**)
10 g	100 ml/1 ml	106–109	oil bath	1 h	61	39	
10 g	100 ml/1 ml	106–109	oil bath	2 h	77	23	
10 g	100 ml/1 ml	106–109	oil bath	3 h	85	15	
10 g	100 ml/1 ml	106–109	oil bath	4 h	95	5	
10 g	100 ml/1 ml	106–109	oil bath	5 h	100	–	43% (4.3 g)
10 g	100 ml/1 ml	106–109	μw	30 min	77	23	
10 g	100 ml/1 ml	106–109	μw	1 h	88	12	
10 g	100 ml/1 ml	106–109	μw	1 h 45	100	–	43% (4.3 g)
10 g	100 ml	106–109	oil bath	1 h	46	54	
10 g	100 ml	106–109	oil bath	2 h	65	35	
10 g	100 ml	106–109	oil bath	3 h	82	18	
10 g	100 ml	106–109	oil bath	4 h	89	11	
10 g	100 ml	106–109	oil bath	5 h	94	6	
10 g	100 ml	106–109	oil bath	6 h 40	100	–	44% (4.4 g)
10 g	100 ml	106–109	μw	30 min	53	47	
10 g	100 ml	106–109	μw	1 h	69	31	
10 g	100 ml	106–109	μw	1 h 30	86	14	
10 g	100 ml	106–109	μw	2 h	94	6	
10 g	100 ml	106–109	μw	2 h 30	96	4	
10 g	100 ml	106–109	μw	2 h 45	100	–	41% (4.2 g)

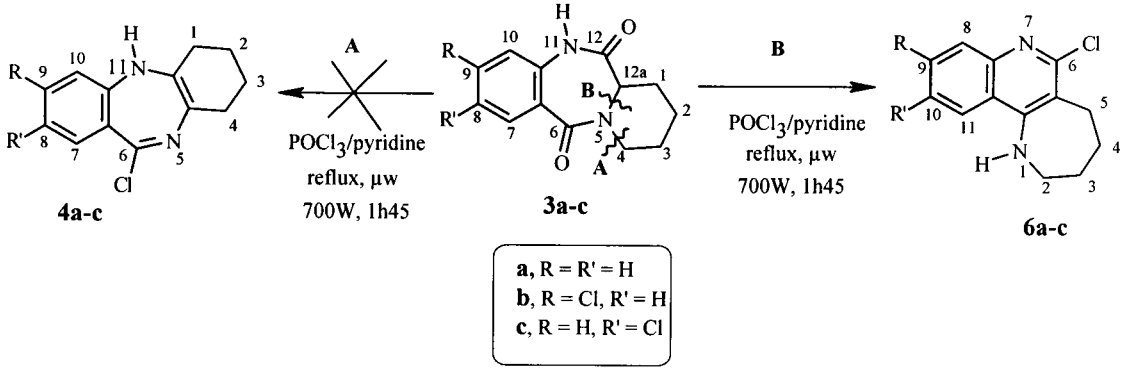
[a] A sample of reaction mixture (≈1 ml) is taken off and excess of $POCl_3$ is immediately destroyed with crushed ice. Then, the residue is treated as depicted in general procedure of the experimental section. Relative percentages of rearranged product and starting material are deduced from NMR spectra.



Scheme 2.

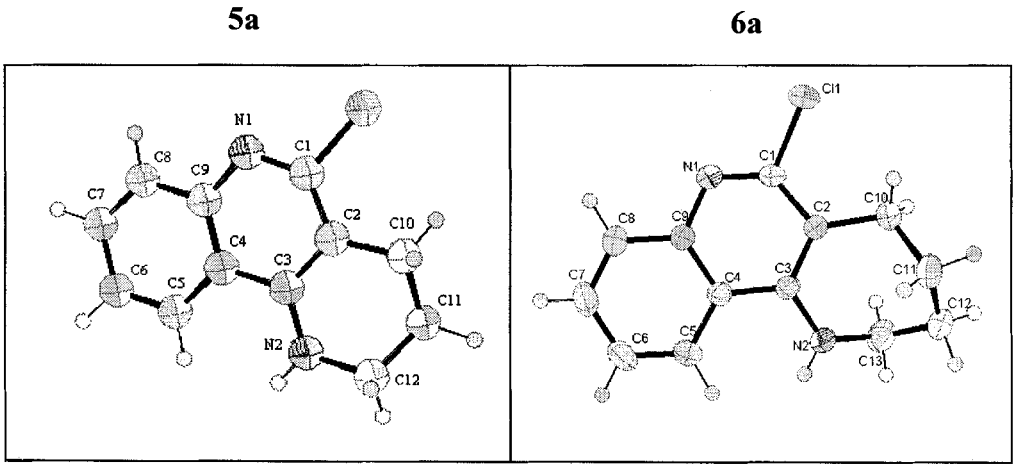
conventional heating conditions, but with a significantly lower rate of reaction. In boiling phosphorus oxychloride, conversion of starting material is obtained in 1 h 45 mn under microwave heating conditions versus 5 h under normal conditions. The presence of a catalytic amount of pyridine accelerates the reaction rate in all cases and the global yield remains the same. All these experimental results were obtained with NMR monitoring at different time of the reaction.

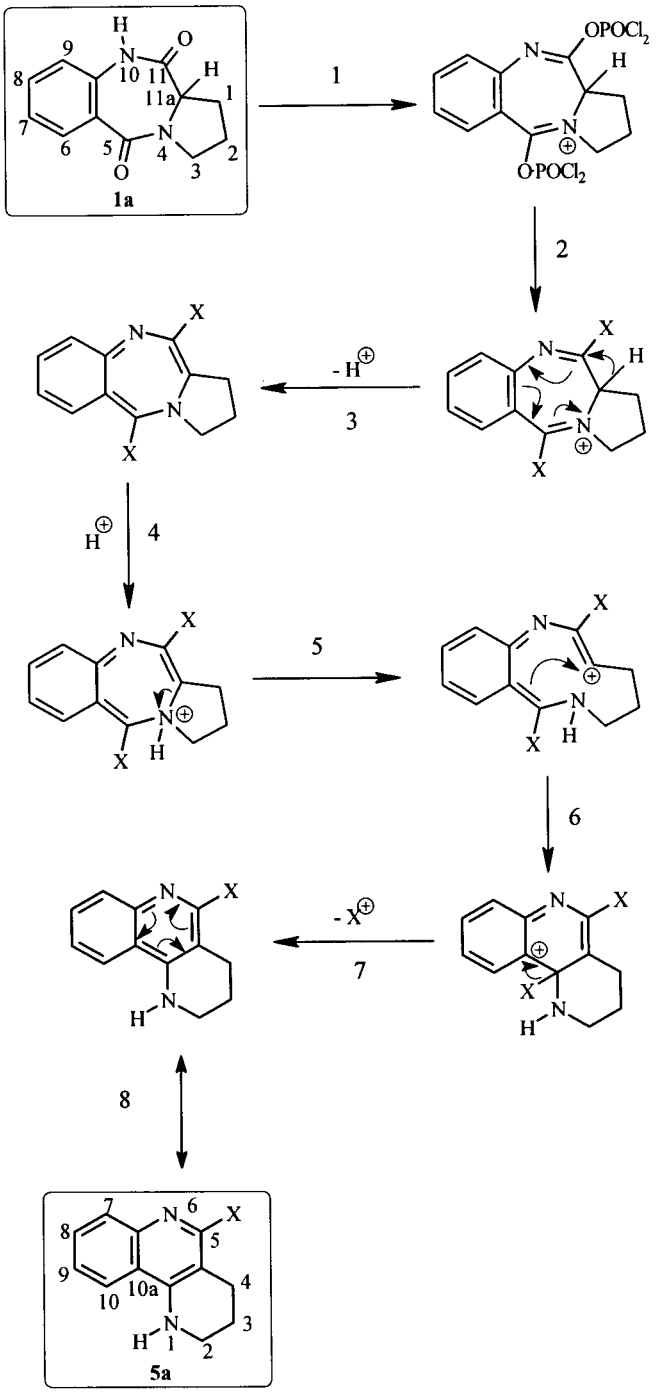
Analytical data (IR, ^{1}H, ^{13}C NMR, MS and elemental analysis) initially led us to propose the structures **2** and **4**



Scheme 3.

Scheme (ORTEP) of crystallographic structures

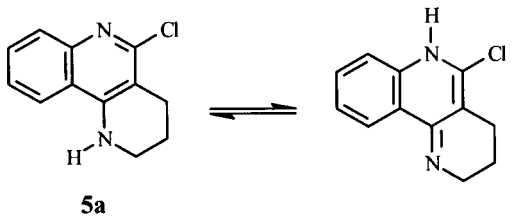




Scheme 4.

for the rearranged products. However, considering the lack of reactivity of N_{10} (**2**) or N_{11} (**4**) amine moiety which could not be acylated or alkylated in standard conditions, and also because the mechanism of this rearrangement which supposed the cleavage of C_3–N_4 link followed by a subsequent recyclisation on C_{11} (**2**) or the cleavage of C_4–N_5 link with subsequent recyclisation on C_{12} (**3**), remained unclear (Scheme 2 and Scheme 3, pathway A) we decided to reinvestigate the structure of compounds **2** and **4** using X-ray diffraction. After several assays, we obtained suitable single crystals of chloroimidates **5a** (ethanol) and **6a** (ether)[5]. These analyses, as depicted in ORTEP schemes of **5a** and **6a**, revealed a quinoleine and not a benzodiazepine skeleton, and assigned the 5-chloro-1,2,3,4-tetrahydrobenzo[*h*][1,6]naphthyridine structure for **5a** obtained from **1a** (Scheme 2, pathway B) and the 6-chloro-2,3,4,5-tetrahydro-1*H*-azepino[3,2-*c*]quinoleine structure for **6a** obtained from **3a** (Scheme 3, pathway B).

The hypothetical mechanism we can now propose is depicted in Scheme 4: the global outcome of this transposition is an oxidation, the rearranged product **5a** having a supplementary sp_2 carbon compared to the dilactam **1a**.



5a

Scheme 5.

This new structure allowed a better understanding of the poor nitrogen N_1 reactivity due to the tautomeric equilibrium as encountered in the 4-aminoquinoleine series[6] (Scheme 5).

However, all these chloroimidates compounds exhibited a good reactivity towards nucleophilic agents. For example, when the chloroimidates **5a** and **6a** were treated with sodium methoxide (3.5 equiv.) in *N*,*N*-dimethylformamide, they gave the methyliminoethers **7a** and **8a** which led to the lactams **9a** and **10a** by treatment with potassium iodide (1.5 equiv.) in acetic acid at 110°C (Scheme 6)[7].

The amidines **11a** and **12a** were synthesized by the treatment of the chloroimidates **5a** and **6a** with *N*-methylpiperazine (10 equiv.) in *N*,*N*-dimethylformamide at 240°C in a sealed tube (Scheme 7).

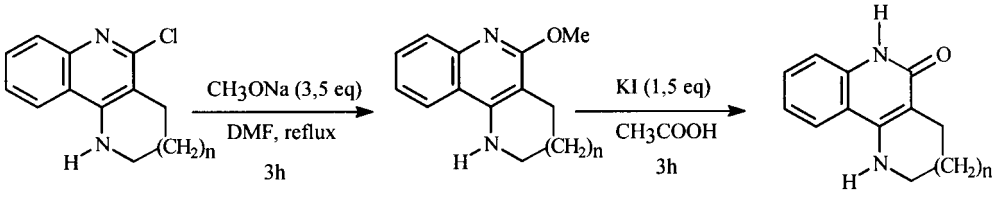
In conclusion, rearrangement of pyrrolo and pyrido[2,1-*c*]-[1,4]benzodiazepines led to new tricyclic systems not yet described in the literature which appear as promising scaffolds in medicinal chemistry[8].

Experimental

General

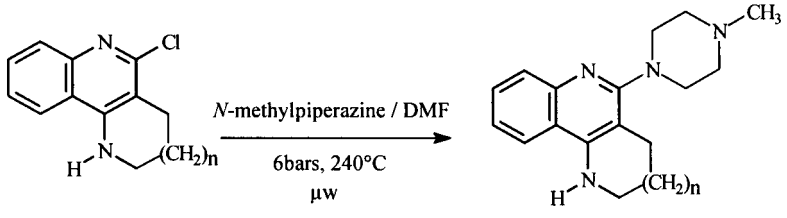
Melting points were determined on a Kofler melting point apparatus and are uncorrected. IR spectra were taken with a Genesis Series FTIR spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a JEOL Lambda 400 spectrometer. Chemical shifts are expressed in parts per million downfield from TMS as the internal standard. Mass spectra (MS) were obtained on a JEOL JMS GCMate spectrometer at an ionizing potential of 70 eV. Elemental analyses were performed at the 'Institut de Recherche en Chimie Organique Fine' (Rouen). Reaction times were monitored by TLC until no starting material remained. Thin-layer chromatography (TLC) were performed on 0.2-mm pre-coated plates of silica gel 60F-264 (Merck). Visualization was made with ultraviolet light. All solvents and reagents were purchased from Acros and Aldrich Chimie and used without further purification.

5-Chloro-1,2,3,4-tetrahydro-benzo[*h*][1,6]naphthyridine (5a). *General procedure*. Method A: A solution of pyrrolo [2,1-*c*][1,4]benzodiazepine-dione **1a** (10 g, 46 mmol) in phosphorus oxychloride (100 ml) and pyridine (1 ml) was heated with stirring under microwave irradiation (700 W) for 1 h 45 min in a Normatron® apparatus. After elimination of $POCl_3$ under reduced pressure, the residue was taken up in water, basified (pH 11) with a 32% ammonia solution and extracted with diethyl ether. The organic layer was evaporated to give a pink solid **5a** (4.4 g, 43%, mp 210°C (ethanol)). Method B: The reaction was carried out under conventional heating for 5 h. IR (KBr) 3300, 1570, 1535, 1420 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.05 (d, 1H, J=8.4 Hz),



5a (n=1) **6a (n=2)** **7a (n=1)** **8a (n=2)** **9a (n=1)** **10a (n=2)**

Scheme 6.



5a (n=1) **6a (n=2)** **11a (n=1)** **12a (n=2)**

Scheme 7.

7.71 (s, 1H, NH), 7.64 (d, 1H, *J*=7.2 Hz), 7.58 (t, 1H, *J*=6.8 Hz), 7.41 (t, 1H, *J*=6.8 Hz), 3.39 (m, 2H), 2.77 (t, 2H, *J*=6.4 Hz), 1.90 (m, 2H). ^{13}C NMR (DMSO-d_6) δ: 151.1, 149.0, 145.9, 129.3, 127.9, 124.4, 121.4, 117.5, 105.5, 40.1, 24.3, 20.2; MS *m*/*z* 220, 218, 183. Anal. Calcd for $C_{12}H_{11}N_2Cl$: C, 65.91; H, 5.07; N, 12.81. Found: C, 66.12; H, 5.08 N, 12.98.

6-Chloro-2,3,4,5-tetrahydro-1*H*-azepino[3,2-*c*]quinoleine (6a). Using the same procedure as described for **5a** (Method A), starting from **3a** (5 g, 26 mmol), we obtained a pink solid **6a** (1.4 g, 28%, mp 218°C (ether)). IR (KBr) 3240, 1560, 1520, 1410, 1370, 1320, 1280, 1220, 1140, 1050, 830 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ:8.15 (d, 1H, *J*=8 Hz), 7.67 (d, 1H, *J*=8 Hz), 7.60 (t, 1H, *J*=7.1 Hz), 7.44 (t, 1H, *J*=7.1 Hz), 7.18 (s, 1H, NH), 3.54 (t, 2H), 3.07 (t, 2H, *J*=5.1 Hz), 1.90 (m, 4H). ^{13}C NMR (DMSO-d_6) δ: 154.2, 152.3, 145.5, 129.2, 127.7, 124.7, 121.4, 119.2, 111.9, 43.6, 27.8, 27.5, 24.3; MS *m*/*z* 234, 232, 190, 163, 127, 104, 88. Anal. Calcd for $C_{13}H_{13}N_2Cl$: C, 67.10; H, 5.63; N, 12.04. Found: C, 66.89; H, 5.32; N, 12.13.

5,8-Dichloro-1,2,3,4-tetrahydro-benzo[*h*][1,6]naphthyridine (5b). The procedure was the same as described for **5a** (Method A). Starting from **1b** (7 g, 28 mmol), a white solid **5b** was obtained (3.4 g, 48%, mp 224°C (ether)). IR (KBr) 3250, 1570, 1530, 1460, 1390, 1330, 1280, 1200, 1170, 1060, 840 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.06 (d, 1H, *J*=7.9 Hz), 7.84 (s, 1H, NH), 7.67 (s, 1H), 7.45 (d, 1H, *J*=7.8 Hz), 3.36 (t, 2H, *J*=6.3 Hz), 2.77 (t, 2H, *J*=6.3 Hz), 1.95 (m, 2H). ^{13}C NMR (DMSO-d_6) δ: 163.7, 150.4, 136.8, 136.2, 131.1, 119.7, 117.6, 113.9, 113.3, 37.3, 35.8, 13.4; MS *m*/*z* 253, 225, 198, 150, 121, 108. Anal. Calcd for $C_{12}H_{10}N_2Cl_2$: C, 56.94; H, 3.98; N, 11.07. Found: C, 56.47; H, 3.95; N, 11.02.

6,9-Dichloro-2,3,4,5-tetrahydro-1*H*-azepino[3,2-*c*]quinoleine (6b). Using the same procedure as described for **5a** (Method A), starting from **3b** (12 g, 45.4 mmol), we obtained a white solid **6b** (5.15 g, 45%, mp 224°C (acetonitrile)). IR (KBr) 3300, 1570, 1520, 1440, 1330, 1270, 1220, 1180, 1090, 950 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.15 (d, 1H, *J*=7.9 Hz), 7.69 (s, 1H), 7.47 (d, 1H, *J*=7.8 Hz), 7.29 (s, 1H, NH), 3.54 (t, 2H, *J*=6.2 Hz), 3.06 (t, 2H, *J*=6.3 Hz), 1.92 (m, 4H). ^{13}C NMR (DMSO-d_6) δ: 163.6, 150.4, 138.8, 136.8, 131.1, 119.7, 117.6, 116.2, 113.3, 34.8, 33.6, 27.1, 26.5; MS *m*/*z* 267, 210, 175, 133, 106, 92. Anal. Calcd for $C_{13}H_{12}N_2Cl_2$: C, 58.40; H, 4.49; N, 10.48. Found: C, 58.06; H, 4.82; N, 10.14.

5,9-Dichloro-1,2,3,4-tetrahydro-benzo[*h*][1,6]naphthyridine (5c). The procedure was the same as described for **5a** (Method A). Starting from **1c** (8 g, 32 mmol), a white solid **5c** was obtained (4.3 g, 53%, mp 230°C (isopropanol)). IR (KBr) 3310, 1580, 1530, 1420, 1360, 1280, 1205, 1170, 1100, 980, 740 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.16 (s, 1H), 7.75 (s, 1H, NH), 7.59 (m, 2H), 3.41 (t, 2H, *J*=6.4 Hz), 2.76 (t, 2H, *J*=6.3 Hz), 1.90 (m, 2H). ^{13}C NMR (DMSO-d_6) δ: 151.5, 148.2, 144.4, 129.9, 129.5, 128.7, 120.6, 118.1, 106.2, 40.1, 24.1, 19.8; MS *m*/*z* 253, 252, 251, 219, 217, 215. Anal. Calcd for $C_{12}H_{10}N_2Cl_2$: C, 56.94; H, 3.98; N, 11.07. Found: C, 56.77; H, 3.84; N, 11.06.

6,10-Dichloro-2,3,4,5-tetrahydro-1*H*-azepino[3,2-*c*]quinoleine (6c). The procedure was the same as described for **5a** (Method A). Starting from **3c** (7 g, 26.5 mmol), we obtained a white solid **6c** (2.8 g, 42%, mp 216°C (isopropanol)). IR (KBr) 3340, 1565, 1520, 1410, 1340, 1260, 1210, 1130, 1020, 840 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.23 (s, 1H), 7.69 (m, 2H), 7.08 (s, 1H, NH), 3.48 (m, 2H), 2.95 (t, 2H, *J*=6 Hz), 1.91 (m, 4H). ^{13}C NMR (DMSO-d_6) δ: 153.4, 152.7, 144.1, 129.8, 129.6, 129.3, 120.8, 120.1, 112.8, 43.5, 27.7, 27.3, 24.2; MS *m*/*z* 267, 266, 251, 238, 231, 203, 140, 84. Anal. Calcd for $C_{13}H_{12}N_2Cl_2$: C, 58.40; H, 4.49; N, 10.48. Found: C, 58.76; H, 4.35; N, 10.26.

5-Methoxy-1,2,3,4-tetrahydro-benzo[*h*][1,6]naphthyridine (7a). To a solution of 5-chloro-1,2,3,4-tetrahydro-benzo[*h*][1,6]naphthyridine **5a** (2 g, 9.2 mmol) in dry *N*,*N*-dimethylformamide (15 ml), sodium methoxide (2 g, 36.6 mmol) was added. The solution was heated under reflux for 3 h. The solvent was removed under reduced pressure and the oily residue was taken up in water (60 ml) and extracted with diethyl ether (2×70 ml). The organic layer was washed with water (2×90 ml), dried with $MgSO_4$, treated with charcoal and evaporated to dryness to give an oil that crystallized in petroleum ether to obtain a yellow powder **7a** (1.3 g, 72%, mp 147°C). IR (KBr) 3250, 1600, 1540, 1370, 1130 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 7.91 (d, 1H, *J*=7.9 Hz), 7.55 (d, 1H, *J*=7.9 Hz), 7.46 (t, 1H, *J*=6.8 Hz), 7,23 (t, 1H, *J*=7.9 Hz), 7.06 (s, 1H, NH), 3.90 (s, 3H, CH_3), 3.34 (t, 2H), 2.61 (t, 2H, *J*=5.9 Hz), 1.85 (m, 2H). ^{13}C NMR (DMSO-d_6) δ: 169.7, 148.9, 136.3, 131.9, 129.6, 122.1, 116.7, 113.8, 112.9, 47.8, 37.1, 36.6, 13.3; Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 73.08; H, 6.25; N, 12.82.

6-Methoxy-2,3,4,5-tetrahydro-1*H*-azepino[3,2-*c*]quinoleine (8a). In the same way as described for **7a**, **8a** was obtained from chloroimidate **6a** (0.7 g, 3 mmol) by refluxing in *N*,*N*-dimethylformamide (7 ml) for 3 h. Extraction gave an oil **8a** (0.53 g, 77%). IR (KBr) 3385, 2942, 2846, 1673, 1567, 1519, 1375, 1211 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.03 (d, 1H, *J*=8.4 Hz), 7.57 (d, 1H, *J*=8.4 Hz), 7.47 (t, 1H, *J*=7.2 Hz), 7.25 (t, 1H, *J*=7.2 Hz), 6.58 (s, 1H, NH), 3.90 (s, 3H, CH_3), 3.33 (t, 2H), 2.88 (t, 2H), 1.83 (m, 4H). Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.41; H, 6.75; N, 12.21.

1,2,3,4,5,6-Hexahydro-benzo[*h*][1,6]naphthyridin-5-one (9a). To a solution of 5-methoxy-1,2,3,4-tetrahydro-benzo[*h*][1,6]naphthyridine **7a** (1 g, 4.67 mmol) in glacial acetic acid (35 ml), potassium iodide (0.90 g, 5.60 mmol) was added. This mixture was heated at 110°C for 3 h. After evaporation of the solvent, the residue was taken up in water and extracted with chloroform (2×60 ml). The organic layer was washed with an aqueous solution of $NaHCO_3$ (2×100 ml) and iodine was removed with an aqueous solution of sodium thiosulfate (3×100 ml). Then, the organic layer was evaporated in vacuo and the solid residue was recrystallised in ether to give a white powder **9a** (0.75 g, 80.3%, mp >260°C). IR (KBr) 3285, 2953, 1640, 1600, 1541, 1472, 1413, 1207 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 10.80 (s, 1H, NH), 7.78 (d, 1H, *J*=7.9 Hz), 7.37 (t, 1H, *J*=7.5 Hz), 7.19 (d, 1H, *J*=7.9 Hz), 7.07 (t, 1H, *J*=7.2 Hz),

6.92 (s, 1H, NH), 3.40 (t, 2H), 2.45 (t, 2H), 1.79 (m, 2H). ^{13}C NMR (DMSO-d_6) δ: 164.6, 147.4, 132.5, 128.0, 118.2, 117.6, 113.8, 112.9, 107.2, 37.0, 36.8, 13.2; MS *m*/*z* 200, 181, 162. Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.13; H, 5.76; N, 13.96.

1,2,3,4,5,6-Hexahydro-7*H*-azepino[3,2-*c*]quinolein-6-one (10a). In the same way as described for **9a**, **10a** was obtained from chloroimidate **8a** (0.45 g, 1.97 mmol) by refluxing in glacial acetic acid (16 ml) for 3 h. Extraction gave a white solid **10a** (0.53 g, 71%, mp >260°C (ether)). IR (KBr) 3361, 2927, 1649, 1603, 1533, 1417, 759 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 10.93 (s, 1H, NH), 7.85 (d, 1H, *J*=7.9 Hz), 7.37 (t, 1H, *J*=7.2 Hz), 7.18 (d, 1H, *J*=7.9 Hz), 7.07 (t, 1H, *J*=7.6 Hz), 6.46 (s, 1H, NH), 3.40 (t, 2H), 2.78 (t, 2H), 1.79 (m, 2H). Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.42; H, 6.54; N, 12.58.

5-(4-Methylpiperazino)-1,2,3,4-tetrahydro-benzo[*h*][1,6]-naphthyridine, dioxalate (11a). *N*-Methylpiperazine (5 ml, 46 mmol) was added to a solution of 5-chloro-1,2,3,4-tetrahydro-benzo[*h*][1,6]naphthyridine **5a** (1 g, 4.6 mmol) in *N*,*N*-dimethylformamide (50 ml). After stirring for 1 h in a sealed tube under microwave heating conditions (240°C, 6 bars, 120 W), the solvent was removed. The residue was taken up in water, extracted with ether (150 ml) and washed with water (2×80 ml). The organic layer was evaporated to give a resulting oil that was taken up in isopropanol (15 ml). This solution was heated under reflux with oxalic acid (5.6 mmol) for 5 min. After cooling, the precipitate was filtered and dried to give **11a** (1.45 g, 68%, mp >260°C (isopropanol)). IR (KBr) 3450, 3160, 1740, 1690, 1630, 1560, 1510, 1420, 1250, 1200, 1130, 1090, 1030, 860 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.04 (d, 1H, *J*=7.9 Hz), 7.71 (d, 1H, *J*=7.9 Hz), 7.59 (t, 1H, *J*=7.5 Hz), 7.36 (t, 1H, *J*=7.7 Hz), 6.96 (s, 1H, NH), 3.41 (m, 4H, 2CH_2), 3.35 (m, 2H), 3.04 (m, 4H, 2CH_2), 2.49 (t, 2H, *J*=6,0 Hz) 2.46 (s, 3H, CH_3), 1.85 (m, 2H). MS *m*/*z* 282, 224, 183, 160, 118, 95, 76. Anal. Calcd for $C_{21}H_{26}N_4O_8$: C, 54.54; H, 5.67; N, 12.12. Found: C, 53.86; H, 5.24; N, 12.14.

6-(4-Methylpiperazino)-2,3,4,5-tetrahydro-1*H*-azepino-[3,2-*c*]quinoleine, trioxalate (12a). Using the same procedure as described for **11a**, starting from the chloroimidate **6a** (0.65 g, 2.8 mmol), we obtained an oily residue. It was dissolved in isopropanol (15 ml). Oxalic acid (6,6 mmol) was added and the mixture warmed under reflux. A yellow precipitate was obtained, collected to give **12a** (0.62 g, 40%, mp 230°C (isopropanol)). IR (KBr) 3412, 2942, 1719, 1620, 1590, 1550, 1410, 1213, 979, 720 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.10 (d, 1H, *J*=8.4 Hz), 7.67 (d, 1H, *J*=8.4 Hz), 7.56 (t, 1H, *J*=7.6 Hz), 7.33 (m, 2H, NH and CH), 3.50 (m, 4H, 2CH_2), 3.28 (m, 2H), 2.82 (m, 4H, 2CH_2), 2.50 (m, 5H, CH_3 and CH_2) 1.88 (m, 4H). MS *m*/*z* 296, 226, 213, 169. Anal. Calcd for $C_{24}H_{30}N_4O_{12}$: C, 50.88; H, 5.34; N, 9.89. Found: C, 50.95; H, 5.74; N, 10.21.

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