NOVEL ENTRY INTO BENZO[*c*]PHENANTHRIDINE SYSTEMS THROUGH A TANDEM ALKENE ACYLATION-CYCLODEHYDRATION

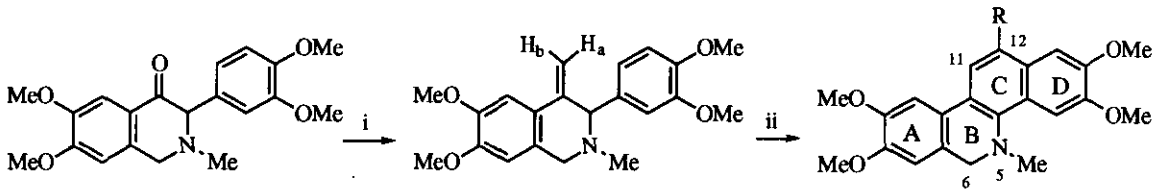
Raul SanMartín, Eduardo Martínez de Marigorta, Isabel Moreno, and Esther Domínguez*

Kimika Organikoa Saila, Zientzi Fakultatea, Euskal Herriko Unibertsitatea, P.O.Box 644 - 48080 Bilbao. Basque Country, Spain

Abstract-12-Alkylbenzo[*c*]phenanthridines have been obtained by an overall high yielding synthetic methodology. Key steps involve Peterson methylenation and an efficient one-pot alkene acylation-cyclization. Smooth oxidation to the benzo[*c*]phenanthridinone system is also reported.

Due to the increasing pharmacological applications of benzo[*c*]phenanthridine alkaloids,[1] the preparation of biologically active compounds as nitidine, fagaronine, etc.[2] and new benzophenanthridine derivatives with potential pharmacological interest has attracted considerable attention from synthetic chemists.[2,3] In the course of our investigations on the applicability of 3-arylisoquinolines towards the synthesis of more complex alkaloid frameworks,[4] we now report an expeditious strategy for the C-ring closure to the benzo[*c*]phenanthridine nucleus.

Following our recent synthesis of 3-aryl-4-isoquinolinone (**1**),[5] we explored the Peterson methylenation[6] of **1**, obtaining the target 4-methylidene derivative (**2**) with good yield. Then it was submitted to olefinic acylation conditions[7] (aliphatic anhydrides, 0.2 M $SnCl_4$ in CH_2Cl_2, reflux), affording directly new 12-alkyl-5,6-dihydrobenzo[*c*]phenanthridines (**3**) (Scheme 1).



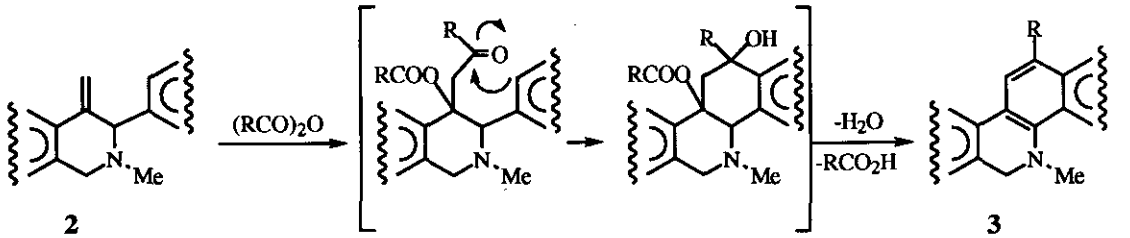
1 **2** (80%)

R= Me **3a** (81%)
R= Et **3b** (79%)
R= *n*-Pr **3c** (85%)

i: 1. Me_3SiCH_2MgCl, THF, reflux ; 2. KH, THF, rt
ii: $(RCO)_2O$, $SnCl_4$, CH_2Cl_2, reflux

Scheme 1

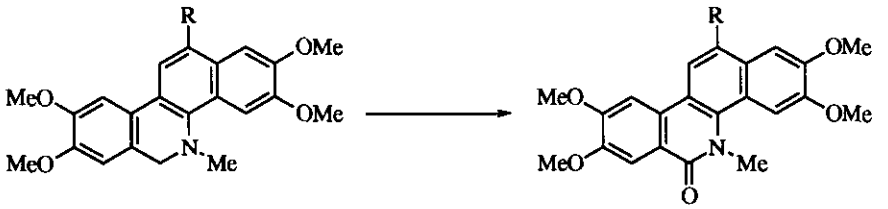
Taking into account previous reports on Friedel-Crafts type acylation reactions,[7,8] we may propose a domino[9] or tandem[10] alkene acylation-cyclodehydration reaction as the most plausible mechanism to explain the formation of the benzo[*c*]phenanthridine framework (Scheme 2).



2 **3**

Scheme 2

With tetracyclic dihydro derivatives (**3a-c**) in hand, a smooth oxidation (activated MnO_2 [4.5 eq.], $CHCl_3$, rt)[11] to the biologically interesting benzo[*c*]phenanthridin-6-one system[3,12] was performed. Thus, 12-alkyl-benzo[*c*]phenanthridin-6(5*H*)-ones (**4a-c**) were obtained regioselectively (Scheme 3).



3

R= Me **4a** (93%)
R= Et **4b** (91%)
R= *n*-Pr **4c** (95%)

Scheme 3

To sum up, we have developed a short and efficient access to benzo[*c*]phenanthridine framework by a synthetic sequence which starting from 3-arylisoquinolinone derivatives involves Peterson methylenation and a novel tandem alkene acylation-cyclodehydration reaction. In addition, the benzo[*c*]phenanthridinone system has been reached smoothly and rapidly by a regioselective oxidation.

EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were obtained by using a Perkin-Elmer 1430 spectrophotometer on KBr pellets or $CHCl_3$ solutions (oils) and peaks (ν) are reported in cm^{-1}. NMR spectra were recorded on a Bruker ACE-250 apparatus at 20-25°C running at 250 MHz for ^1H and 62.8 MHz for ^{13}C in $CHCl_3$ (7.26 ppm) as an internal reference in $CDCl_3$ solutions. Chemical shifts (δ) are given in ppm; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet) or dd (doublet of doublets). Coupling constants (J) are reported in

hertz (Hz). ^{1}H-{^{1}H} NOE experiments were carried out in the difference mode by irradiation of all the lines of a multiplet in $CDCl_3$ solvent.[13] Assignment of individual ^{13}C resonances were supported by DEPT experiments.[14] Combustion analyses were performed with a Perkin-Elmer 2400 CHN apparatus. MS (EI) were obtained on a MS902 model Kratros apparatus. Data are reported in the form m/z (intensity relative to base = 100). Tetrahydrofuran (THF) was freshly distilled from benzophenone-sodium ketyl. All other solvents used were technical grade and purified according to standard procedures.[15] TLC was performed on silica gel 60 F_{254} plates and visualized by UV light (254 nm) or Dragendorff's reagent.[16] Flash column chromatography[17] was performed on Merck kieselgel 60 (230-400 mesh ASTM); air-pressure chromatography was carried out on Merck kieselgel 60 (70-230 mesh ASTM). The reactions were carried out under an atmosphere of dry, deoxygenated argon unless otherwise indicated. All transfers of liquid solutions and solvents were performed by syringe techniques or *via canula*.[18]

6,7-Dimethoxy-3-(3,4-dimethoxyphenyl)-*N*-methyl-4-methyliden-1,2,3,4-tetrahydroisoquinoline (2). Me_3SiCH_2MgCl (50 mL of a 1M solution in THF,[19] 50 mmol) was added dropwise to solid isoquinolinone (**1**) (0.12 g, 0.33 mmol) under nitrogen at 0°C. After refluxing (90°C) for 1 h, the mixture was cooled to 0°C and a saturated solution of NH_4Cl in water (10 mL) was added dropwise. The aqueous layer was extracted with ether (5 x 20 mL) and the combined organic layers were dried over anhydrous sodium sulfate. Evaporation *in vacuo* afforded a yellow oil which was dissolved in methanol/dichloromethane (0.5:9.5), filtered through silica gel (70-230 mesh ASTM), and evaporated *in vacuo*. The resulting syrup was dissolved in dry THF (3 mL) under nitrogen at room temperature, then added to a stirred suspension of KH (35% in paraffin oil, previously washed with hexane, 1.32 g, ~33 mmol) in dry THF (10 mL). After stirring for 6 h, the mixture was cooled to 0°C and a saturated solution of NH_4Cl in water (10 mL) was added dropwise. The aqueous layer was extracted with ether (5 x 20 mL) and the combined organic layers were dried over anhydrous sodium sulfate. Evaporation *in vacuo* afforded a brown solid which was purified by air pressure column chromatography using methanol/ethyl acetate (0.1:9.9) as eluent. The alkene (**2**) was obtained (0.09 g, 80 %) as a colourless oil, R_f (5% MeOH/CH_2Cl_2) 0.6. IR ($CHCl_3$): ν 1606 (C=C st.). ^{1}H-NMR: δ 2.36 (3H, s, NMe); 3.50 (1H, d, *J* 15.7, H-$1_{pseudo\text{-}ax}$); 3.79 (3H, s, OMe); 3.80 (1H, d, *J* 15.7, H-$1_{pseudo\text{-}eq}$); 3.81 (3H, s, OMe); 3.84 (3H, s, OMe); 3.90 (3H, s, OMe); 4.22 (1H, s, H-3); 4.79 (1H, s, H_a); 5.63 (1H, s, H_b); 6.50 (1H, s, H-8_{arom}); 6.75 (2H, s, H_{arom}); 6.89 (1H, s, H_{arom}); 7.17 (1H, s, H-5_{arom}). ^{13}C-NMR: δ 42.8 (NMe); 53.5 (C-1); 55.7, 55.8 (OMe); 69.9 (C-3); 106.1, 108.8 (C_{arom}-H); 109.7 (=CH_2); 110.4, 111.7, 120.9 (C_{arom}-H); 124.6, 126.1, 132.4 eta 140.9 (C_{arom}-C, C-4); 148.0, 148.2, 148.8, eta 149.3 (C_{arom}-O). MS: (m/z, %) 355 (M^+, 10); 354 (11); 218 (49); 180 (100). *Anal.* Calcd for $C_{21}H_{25}NO_4$: C, 70.95; H, 7.09; N, 3.90. Found: C, 70.91; H, 7.10; N, 3.96.

5,12-Dimethyl-2,3,8,9-tetramethoxy-5,6-dihydrobenzo[*c*]phenanthridine (3a). Typical procedure. $SnCl_4$ (2.8 mL of a 0.2 M solution in dichloromethane) was added dropwise to a stirred solution of alkene (**2**) (0.03 g, 0.09 mmol) and acetic anhydride (1.6 mL, 0.28 mmol) in dry

dichloromethane (1 mL) under nitrogen at 0°C. After heating to 40°C for 15 h, the reaction mixture was cooled to 0°C and ice (~0.3 g) was added. Evaporation *in vacuo* (temperature < 50°C) afforded a brown oil which was dissolved in methanol (1 mL), water (50 mL) and HCl (5 mL of a 1 M solution in water). The aqueous solution was washed with hexane (2 x 10 mL), basified to pH 10 with a saturated solution of K_2CO_3 in water and extracted with hexane (10 x 15 mL) and ether (2 x 5 mL). The combined organic layers were dried over anhydrous sodium sulfate and evaporated *in vacuo* to give a brown oil which was purified by air pressure column chromatography using methanol/dichloromethane (0.1:9.9) as eluent. The 12-methylated benzo[*c*]phenanthridine derivative (**3a**) was obtained (0.03 g, 81%) as a white powder, mp 126-128°C (hexane), R_f (5%MeOH/CH_2Cl_2) 0.9. IR ($CHCl_3$): ν 1601 (C=C st.). ^{1}H-NMR: δ 2.60 (3H, s, NMe); 2.68 (3H, s, C_{12}Me); 3.95 (3H, s, OMe); 4.01 (3H, s, OMe); 4.04 (3H, s, OMe); 4.07 (3H, s, OMe); 4.14 (2H, s, H-6); 6.80 (1H, s, H-7); 7.21 (1H, s, H-1); 7.32 (1H, s, H-10); 7.55 (1H, s, H-11); 7.70 (1H, s, H-4). ^{13}C-NMR: δ 19.7 ($C_{12}CH_3$); 40.9 (NMe); 55.6 (C-6); 55.8, 55.9, 56.0, 56.2 (OMe); 103.3, 103.7, 106.2, 110.2, 120.4 (C_{arom}-H); 123.6, 124.3, 124.8, 125.1, 128.4, 129.2 (C_{arom}-C); 140.7 (C_{arom}-N); 148.5, 148.6, 149.2, 149.4 (C_{arom}-O). MS: (m/z, %) 380 (M+1, 18); 379 (M^+,85); 378 (100); 363 (67); 362 (40); 189 (18). *Anal.* Calcd for $C_{23}H_{25}NO_4$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.71; H, 6.67; N, 3.66.

When the same procedure was performed on alkene (**2**) (0.05 g, 0.14 mmol) using propionic anhydride as reagent, **12-ethyl-5-methyl-2,3,8,9-tetramethoxy-5,6-dihydrobenzo[*c*]phenanthridine (3b)** was obtained (0.04 g, 79%) as a white powder, mp 176-178°C (hexane), R_f (5%MeOH/CH_2Cl_2) 0.9. IR ($CHCl_3$): ν 1603 (C=C st.). ^{1}H-NMR: δ 1.44 (3H, t, *J* 7.5, CH_2CH_3); 2.60 (3H, s, NMe); 3.09 (2H, q, *J* 7.5, CH_2Me); 3.95 (3H, s, OMe); 4.01 (3H, s, OMe); 4.03 (3H, s, OMe); 4.07 (3H, s, OMe); 4.14 (2H, s, H-6); 6.80 (1H, s, H-7); 7.28 (1H, s, H-1); 7.33 (1H, s, H-10); 7.56 (1H, s, H-11); 7.71 (1H, s, H-4). ^{13}C-NMR: δ 14.9 (CH_2CH_3); 26.3 (CH_2Me); 40.8 (NMe); 54.8 (C-6); 55.7, 55.8, 55.9, 56.1 (OMe); 103.3, 103.4, 106.1, 110.0, 118.7 (C_{arom}-H); 123.5, 124.3, 125.0, 125.1, 127.5, 135.2 (C_{arom}-C); 140.5 (C_{arom}-N); 148.4, 148.5, 149.0, 149.2 (C_{arom}-O). MS: (m/z, %) 393 (M^+,29); 392 (100); 377 (28); 376 (21); 196 (10). *Anal.* Calcd for $C_{24}H_{27}NO_4$: C, 72.79; H, 6.68; N, 3.68. Found: C, 72.77; H, 6.68; N, 3.68.

When the same procedure was performed on alkene (**2**) (0.05 g, 0.14 mmol) using butyric anhydride as reagent, **5-methyl-12-*n*-propyl-2,3,8,9-tetramethoxy-5,6-dihydrobenzo[*c*]phenanthridine (3c)** was obtained (0.05 g, 85%) as a white powder, mp 130-132°C (decomp) (hexane), R_f (5%MeOH/CH_2Cl_2) 0.9. IR ($CHCl_3$): ν 1603 (C=C st.). ^{1}H-NMR: δ 1.08 (3H, t, *J* 7.4, CH_2CH_3); 1.83 (2H, m, CH_2Me); 2.60 (3H, s, NMe); 3,02 (2H, t, *J* 7.4, $C_{12}CH_2$); 3.95 (3H, s, OMe); 4.02 (3H, s, OMe); 4.03 (3H, s, OMe); 4.07 (3H, s, OMe); 4.14 (2H, s, H-6); 6.80 (1H, s, H-7); 7.27 (1H, s, H-1); 7.32 (1H, s, H-10); 7.54 (1H, s, H-11); 7.71 (1H, s, H-4). ^{13}C-NMR: 14.4 (CH_2CH_3); 23.7 (CH_2Me); 35.5 ($C_{12}CH_2$); 40.8 (NMe); 55.0 (C-6); 55.8, 55.9, 56.0, 56.2 (OMe); 103.4, 106.3, 110.2, 119.8, 123.5 (C_{arom}-H); 124.5, 125.2, 127.8, 133.8 (C_{arom}-C); 140.7 (C_{arom}-N); 148.5, 148.6, 149.1, 149.3 (C_{arom}-O). MS: (m/z, %) 408 (M+1, 25); 407 (M^+,100); 406 (70); 378 (39); 362 (12).

Anal. Calcd for $C_{25}H_{29}NO_4$: C, 73.67; H, 7.18; N. 3.44. Found: C, 73.62; H, 7.19; N, 3.47.

5,12-Dimethyl-2,3,8,9-tetramethoxybenzo[*c*]phenanthridin-6(5*H*)-one (4a). Typical procedure. Activated MnO_2 (0.11 g, 1.3 mmol) was added to a stirred solution of 5,6-dihydrobenzo[*c*]phenanthridine (**3a**) (0.1 g, 0.26 mmol) in dry chloroform (3 mL) under nitrogen at room temperature. After stirring for 36 h, the mixture was filtered and the filtrate was evaporated *in vacuo* to give a brown oil which was purified by air pressure column chromatography using methanol/dichloromethane (0.2:9.8) as eluent. The benzo[*c*]phenanthridinone (**4a**) was obtained (0.095 g, 93%) as a white powder, mp 138-140°C (hexane), R_f (5%MeOH/CH_2Cl_2) 0.8. IR ($CHCl_3$): ν 1633 (C=O st.). ^{1}H-NMR: δ 2.74 (3H, s, C_{12}Me); 4.02 (3H, s, OMe); 4.04 (3H, s, OMe); 4.06 (3H, s, OMe); 4.07 (3H, s, OMe); 4.12 (3H, s, NMe); 7.27 (1H, s, H-1); 7.61 (1H, s, H-10); 7.64 (1H, s, H-4); 7.84 (1H, s, H-11); 7.94 (1H, s, H-7). ^{13}C-NMR: 19.7 ($C_{12}CH_3$); 41.0 (NMe); 55.8, 55.9, 56.2 (OMe); 102.7, 103.7, 105.8, 108.7, 115.9 (C_{arom}-H); 118.7, 119.2, 120,0, 128.3, 129.5, 134.0 (C_{arom}-C, C_{arom}-N); 147.7, 149.1, 149.5, 153.4 (C_{arom}-O); 164.4 (C=O). MS: (m/z, %) 394 (M+1, 33); 393 (M^+,100); 378 (38). *Anal.* Calcd for $C_{23}H_{23}NO_5$: C, 70.20; H. 5.89; N, 3.56. Found: C, 70.23; H, 5.88; N, 3.59.

When the same procedure was applied to 5,6-dihydrobenzo[*c*]phenanthridine (**3b**) (0.1 g, 0.25 mmol) **12-ethyl-5-methyl-2,3,8,9-tetramethoxybenzo[*c*]phenanthridin-6(5*H*)-one (4b)** was obtained (0.09 g, 91%) as a white powder, mp 165-167°C (hexane), R_f (5%MeOH/CH_2Cl_2) 0.7. IR ($CHCl_3$): ν 1638 (C=O st.). ^{1}H-NMR: δ 1.48 (3H, t, *J* 7.5, CH_2CH_3); 3.14 (2H, q, *J* 7.5, CH_2Me); 4.02 (3H, s, OMe); 4.04 (3H, s, OMe); 4.06 (3H, s, OMe); 4.07 (3H, s, OMe); 4.13 (3H, s, NMe); 7.35 (1H, s, H-1); 7.62 (2H, s, H-10 and H-4); 7.84 (1H, s, H-11); 7.95 (1H, s, H-7). ^{13}C-NMR: 14.9 (CH_2CH_3); 26.4 (CH_2Me); 41.2 (NMe); 55.8, 56.1, 56.2 (OMe); 102.6, 103.4, 105.9, 108.6 (C_{arom}-H); 119.2, 120.3, 128.6, 129.0, 133.9, 134.4 (C_{arom}-C, C_{arom}-N); 147.6, 149.1, 149.4, 153.4 (C_{arom}-O); 164.4 (C=O). MS: (m/z, %) 408 (M^+,26); 407 (100); 393 (20); 392 (79). *Anal.* Calcd for $C_{24}H_{25}NO_5$: C, 70.73; H, 6.19; N, 3.44. Found: C, 70.77; H, 6.11; N, 3.43.

When the same procedure was applied to 5,6-dihydrobenzo[*c*]phenanthridine (**3c**) (0.1 g, 0.24 mmol) **5-methyl-12-*n*-propyl-2,3,8,9-tetramethoxybenzo[*c*]phenanthridin-6(5*H*)-one (4c)** was obtained (0.098 g, 95%) as a white powder, mp 182-184°C (hexane), R_f (5%MeOH/CH_2Cl_2) 0.7. IR ($CHCl_3$): ν 1636 (C=O st.). ^{1}H-NMR: δ 1.11 (3H, t, *J* 7.3, CH_2CH_3); 1.87 (2H, m, CH_2Me); 3.08 (2H, t, *J* 7.4, $C_{12}CH_2$); 4.02 (3H, s, OMe); 4.04 (3H, s, OMe); 4.06 (6H, s, OMe); 4.14 (3H, s, NMe); 7.33 (1H, s, H-1); 7.61 (2H, s, H-10 and H-4); 7.82 (1H, s, H-11); 7.94 (1H, s, H-7). ^{13}C-NMR: 14.1 (CH_2CH_3); 23.6 (CH_2Me); 35.6 ($C_{12}CH_2$); 41.2 (NMe); 55.8, 55.9, 56.1 (OMe); 102.6, 103.5, 105.8, 108.6 (C_{arom}-H); 115.9 (C_{arom}-C); 119.2, 120.4, 128.8, 129.0, 132.9, 134.0 (C_{arom}-C, C_{arom}-N); 147.6, 149.1, 149.5, 153.4 (C_{arom}-O); 164.4 (C=O). MS: (m/z, %) 422 (M+1, 29); 421 (M^+,100); 393 (25); 392 (89); 376 (11). *Anal.* Calcd for $C_{25}H_{27}NO_5$: C, 71.23; H, 6.46; N, 3.32. Found: C, 71.20; H, 6.38; N, 3.41.

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