An Expedient Phase Transfer Catalyst-Mediated Synthesis of 2-Alkyl/Aryl-1,8-phenanthrolines

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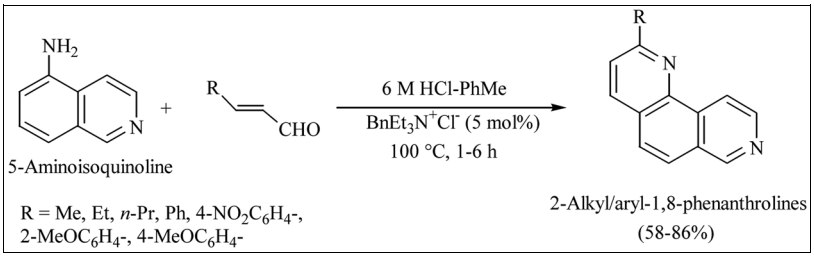

Several 2-alkyl and 2-aryl-1,8-phenanthrolines were synthesized efficiently from 5-aminoisoquinoline and seven α,β-unsaturated aldehydes in aq. HCl–toluene mixture at 100°C using benzyltriethylammonium chloride as a phase transfer catalyst.

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INTRODUCTION

During the last decade, we have been engaged in developing newer syntheses of condensed nitrogen heterocycles [1]. Our ongoing interest drew our attention to phenanthrolines [2] primarily, because many members of the five out of 10 possible isomeric phenanthrolines are bioactive. We were specially interested in 1,8-phenanthrolines, because, besides being bioactive, these molecules appeared to be interesting from synthetic point of view.

Thus, regarding the bioactivities, 1,8-phenanthroline itself inhibits incorporation of proline into proteins, the 8-oxide is antibacterial [2], certain bromo derivatives [3] and some *N*-methyl-1,8-phenanthrolinium salts [4] are fungicidal and bactericidal, several (*N*,*N*-diethylamino)-alkoxy derivatives are DNA-binding agents [5], the benzo [*b*] derivatives are amoebicides [6], and benzo[*c*] derivatives are cytotoxic, DNA-intercalators, and inhibitors of topoisomerase I [7].

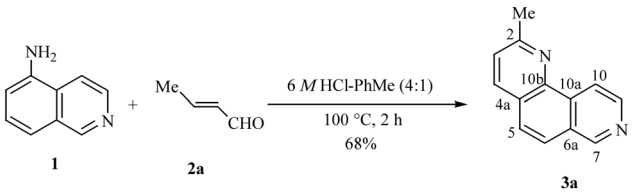
As regards their syntheses reported after the early synthesis of 2,3-diphenyl-1,8-phenanthroline by the Doebner pyruvic acid reaction [8]8, nearly all the methods suffered from cognizable shortcomings like low yields (e.g., 5%) of the products [9] and the use of strong mineral acid (e.g., conc. H_2SO_4; refs. 9 and 10) and toxic arsenic compounds (e.g., H_3AsO_4; refs. [9] and [10]), and As_2O_5 [11]. A latter, somewhat improved but multistep synthesis of 3,4-disubstituted 1,8-phenanthrolines [12] notwithstanding, this situation called for the development of a short synthesis which would be void of these difficulties. We have indeed been able to achieve this goal by the application of Skraup/Doebner–von Miller reaction [13] between 5-aminoisoquinoline and a number of α,β-unsaturated aldehydes but by carrying out the reactions in a biphasic reaction medium (6*M* HCl–toluene) containing a phase transfer catalyst (PTC). As a result, a number of 2-alkyl and 2-aryl-1,8-phenanthrolines were synthesized in moderate to very good yields. The outcome of our successful venture is presented below.

RESULTS AND DISCUSSION

As the Skraup/Doebner–von Miller reaction requires the use of a strong acid, we initially tried montmorillonite K10 clay, a well-known environmentally benign acidic substance [14] in this reaction using microwave irradiation (MWI) as an alternate source of energy [15] with a view to develop a green synthesis. Accordingly, 5-aminoisoquinoline **1** was prepared from 5-nitroisoquinoline, procured commercially, by reduction with palladized charcoal and hydrazine hydrate [16]. It was then treated with an equimolar amount of crotonaldehyde **2a**, adsorbed on montmorillonite K10 clay, under MWI (70% power; 560 W) for 12 min (6 × 2-min pulses) in a solvent-free manner. But the amine still remained largely unconsumed. The amine was not fully consumed even when two equivalents of **2a** were used in a separate experiment (not described in Experimental section). Thus, this approach failed.

Next, **1** was heated with two equivalents of **2a** in HCl (6*M*)-toluene (4:1) at 100°C, until (2 h) the amine was fully consumed. A single product was formed. It was isolated in 68% yield after a simple work-up, followed by chromatography over a column of silica gel, and identified as the known 2-methyl-1,8-phenanthroline **3a** by comparison (melting point [9] and supportive ^1H and ^{13}C NMR data). The reaction is represented in Scheme 1.

Scheme 1



As the yield of **3a** was only moderate, we tried to improve upon the yield by carrying out the reaction separately in the presence of 5 mol % of six different PTCs, namely, benzyltriethylammonium chloride (BTEAC), Adogen-464, benzyldimethylhexadecylammonium chloride (BDHC), cetylpyridinium bromide (CPB), cetyltrimethylammonium bromide (CTAB), and tetra-*n*-butylammonium bromide (TBAB). The results are shown in Table 1.

Clearly, the reaction was not only more expeditious but also furnished **3a** in a much higher yield (86%), when BTEAC was used as the PTC. To find out the appropriate catalytic and acidic concentrations, the reaction between **1** and **2a** was repeated separately using (i) 10 mol % of BTEAC in 6*M* HCl–PhMe (4:1) and (ii) 5 mol % of BTEAC in 12*M* HCl–PhMe (4:1), both at 100°C. Both the reactions were complete in 1 h but furnished **3a** in 74 and 55% yields, respectively. Obviously, 5 mol % of BTEAC in 6*M* HCl–PhMe (4:1) was a better option in this reaction.

Consequently, these conditions were used in all subsequent reactions. Thus, **1** was separately treated with seven other α,β-unsaturated aldehydes **2b–h** under the conditions stated above. Only 2-nitrocinnamaldehyde **2e** did not react even after 8 h. The rest of the substrates took 1–6 h for completion and furnished a single product in each case. These products were purified by column chromatography and identified spectroscopically (IR, ^{1}H, and ^{13}C NMR, GC EI-MS, elemental analysis) as the expected 2-alkyl-1,8-phenanthrolines **3b**,**c** and the 2-aryl-1,8-phenanthrolines **3d**,**f–h**. The reactions, including that of **1** with **2a**, are shown in Scheme 2, and the results are listed in Table 2.

Till the time of our taking up this work, there existed a few reports on the ^{1}H and ^{13}C NMR spectroscopic data of 1,8-phenanthroline itself [17,18]. But such data on 2-substituted 1,8-phenanthrolines were, to the best of our knowledge, lacking. We, therefore, determined the definitive ^{1}H and ^{13}C chemical shifts of two representative members, namely, **3a** and **3d** by analyzing their heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond correlation (HMBC) spectra and deduced the same for the rest by comparing their NMR data with those of **3a** and **3d**. Since there was a good agreement amongst the two sets of values, the individual ^{1}H and ^{13}C NMR chemical shift ranges for all the products were easily ascertained (see Experimental section). These data unveiled certain NMR characteristics, stated below, which are useful in identifying and determining the individual NMR assignments of 2-alkyl and 2-aryl-1,8-phenanthrolines.

Regarding the ^{1}H NMR assignments, the chemical shifts of ring C protons are totally unaffected by the substituents at C-2. Thus, H-7, H-10, and H-9 appear at δ 9.25–9.45 (s), 9.0–9.2 (d, J = 5.5 Hz), and 8.8–8.9 (d, J = 5.5 Hz), respectively. For 2-alkylphenanthrolines, the protons of rings A and B are distinguishable, as they appear at about δ 7.5 (H-3), 7.75 (H-5), 7.8 (H-6), and 8.1 (H-4) (d each, J = 8–9 Hz). However, for 2-arylphenanthrolines, these protons cannot be distinguished, and they appear at δ 7.8–8.7 (d each, 1H, J = 8–9 Hz).

As regards the ^{13}C NMR data, C-2, C-10a, and C-10b appear at about δ 160 ± 4, 136, and 145, respectively, whereas C-4a appear at about δ 127 and C-6a at about δ 129. The difference between the chemical shifts of C-4a

Scheme 2

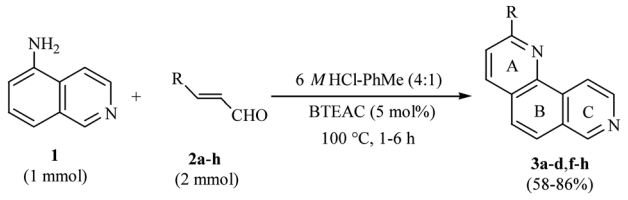


Table 1

Effect of different PTCs on the reaction of **1** with **2a** in 6*M* HCl–PhMe at 100°C.

Entry	Catalyst (5 mol %)	Time (h) of reaction	Yield (%) of **3a**
1	BTEAC	1.0	86
2	Adogen-464	1.0	59
3	BDHC	1.0	72
4	CPB	2.0	54
5	CTAB	4.0	34
6	TBAB	2.0	48

Table 2

Reaction of **1** with **2a–h** using BTEAC (5 mol %) in 6*M* HCl—PhMe at 100°C.

Entry	*E*-RCH CHCHO (**2**): R =	Time (h) of reaction	Product[a] (**3**)	Yield (%) of **3**
1	**a**: Me	1	**a**	86
2	**b**: Et	2	**b**	84
3	**c**: *n*-Pr	2	**c**	79
4	**d**: Ph	5	**d**	60
5	**e**: 2-$NO_2C_6H_4$	8	N.R.	–
6	**f**: 4-$NO_2C_6H_4$	6	**f**	58
7	**g**: 2-$MeOC_6H_4$	3	**g**	69
8	**h**: 4-$MeOC_6H_4$	3	**h**	76

N.R.: No reaction.
[a]Except **3a**, all were new compounds.

and C-6a, though marginal, is observed in all the compounds. The chemical shifts of CH-4 (δ 136 ± 1), CH-5 (δ 127), CH-7 (δ 151+), CH-9 (δ 146), and CH-10 (δ 118) are distinct and well separated. However, those of CH-3 (*ca.* δ 121–125) and CH-6 (*ca.* δ 125) are close.

To our knowledge, the present synthesis constitutes the first PTC-mediated Skraup/Doebner–von Miller synthesis of the 1,8-phenanthroline skeleton—2-alkyl and 2-aryl derivatives, to be precise. The reactions do not involve any toxic substance, the reaction periods are not too long (1–6 h), and the yields of the products are acceptable (58–86%), which renders the present method useful.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. FT-IR (KBr) spectra were recorded in a Perkin-Elmer RX 1 FT-IR spectrophotometer, NMR (recorded in $CDCl_3$, unless stated otherwise; ^1H, 500 MHz; ^{13}C, 125 MHz; DEPT 135, HMQC, and HMBC) in a Bruker DRX-500 spectrometer, the GC EI-MS spectra in a Thermo Scientific Trace GC Ultra—PO-LARIS Q 230LT mass spectrometer and elemental analyses in a Perkin Elmer 2400 Series II C, H, N Analyzer. The analytical thin layer chromatographies were carried out on silica gel G (Merck, India) plates and column chromatographies on silica gel (60–120 mesh, Qualigens, India). PE refers to petroleum ether, bp 60–80°C, and DCM stands for dichloromethane. MWI was carried out using a domestic BPL SANYO microwave oven (800 W).

5-Aminoisoquinoline (1). A solution of 5-nitroisoquinoline (0.35 g, 2 mmol) in EtOH (20 mL) containing $NH_2NH_2{\cdot}H_2O$ (2 mmol) and 10% Pd/C (10% w/w; 0.035 g) was refluxed on steam-bath for 30 min. The solution was filtered hot through a bed of Celite®, washed with hot ethanol (2×10 mL), solvent distilled from the pooled filtrates, and the resulting residue crystallized from PE–DCM to furnish pure **1** as orange-yellow needles, 0.282 g (98%), mp 127–128°C (lit. mp [19] 128–129°C).

General procedure for preparation of 2-substituted 1,8-phenanthrolines. The araldehyde **2a–h** (2 mmol) was added dropwise/portionwise with stirring to a warm solution of **1** (1 mmol) in 6*M* aq. HCl (6 mL)-PhMe (1.5 mL) containing 5 mol % BTEAC and heated at 100°C until (1–6 h), the amine was consumed. The solution was cooled to r.t. and diluted with water (10 mL) and EtOAc (10 mL). In some cases, turbidity appeared during dilution with water, when dil. HCl was added until the turbidity disappeared. The EtOAc layer was separated and washed with water (2× 5 mL). The pooled aqueous extracts were basified (pH *ca*. 8–9) with 10% aq. NaOH in cold and extracted with EtOAc (3× 10 mL). The organic layer was washed with water, dried, and the solvent distilled off. The resulting residue was purified by CC and eluted with 8–20% PE-EtOAc to furnish pure **3a–d**,**f–h**. The solid products **3a**,**d**,**f**, **g**,**h** were further purified by crystallization.

2-Methyl-1,8-phenanthroline (3a). Light brown needles (PE–DCM), 0.167 g (86%), mp 98–99°C (lit. mp [9] 97–99°C); IR: 1585, 1507, 1440, 1383, 1030, 854, 812, 730 cm^{-1}; ^1H NMR: δ 2.84 (s, 3H, CH_3), 7.48, 7.75, 7.81, and 8.09 (d, each, 1H, H-3, H-5, H-6, and H-4, respectively, J = 8.5 Hz), 8.81 and 9.02 (d, each, 1H, H-9, and H-10, respectively, J = 5.5 Hz), 9.27 (s, 1H, H-7); ^{13}C NMR: δ 25.7 (CH_3), 117.7 (CH-10), 124.4 and 124.8 (CH-3,6), 126.4 (C-4a), 127.2 (CH-5), 128.8 (C-6a), 136.0 (C-10a), 136.4 (CH-4), 144.7 (C-10b), 145.6 (CH-9), 151.3 (CH-7), 159.1 (C-2); GC EI-MS: *m*/*z* (%) 194 (M^+, 100), 193 (40), 167 (26), 166 (13). Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.41; H, 5.15; N, 14.43. Found: C, 80.47; H, 5.18; N, 14.40.

2-Ethyl-1,8-phenanthroline (3b). Light yellow liquid, 0.175 g (84%); IR: 1588, 1559, 1507, 1441, 1387, 1037, 854, 814 cm^{-1}; ^1H NMR: δ 1.48 (t, 3H, J = 7.5 Hz), 3.11 (q, 2H, J = 7.5 Hz), 7.50 (d, 1H, J = 8.0 Hz), 7.75 and 7.81 (d, each, 1H, J = 8.5 Hz), 8.11 (d, 1H, J = 8.0 Hz), 8.81 and 9.06 (d, each, 1H, J = 5.5 Hz), 9.27 (s, 1H); ^{13}C NMR: δ 14.0 (CH_3), 32.4 (CH_2), 117.8, 123.5, 124.8, 127.3, 136.4, 145.6, 151.3 (all Ar-CH), 126.6, 128.8, 136.2, 144.6, 163.9 (all Ar-C); GC EI-MS: *m*/*z* (%) 208 (M^+, 66), 207 (100). Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.77; H, 5.77; N, 13.46. Found: C, 80.82; H, 5.75; N, 13.49.

2-*n*-Propyl-1,8-phenanthroline (3c). Light yellow liquid, 0.176 g (79%); IR: 1586, 1559, 1507, 1441, 1386, 1036, 853, 814 cm^{-1}; ^1H NMR: δ 1.06 (t, 3H, J = 7.5 Hz), 1.95 (sextet, 2H, J = 7.5 Hz,), 3.05 (t, 2H, J = 7.5 Hz), 7.47, 7.74, 7.80, and 8.09 (d, each, 1H, J = 8.5 Hz), 8.80 and 9.05 (d, each, 1H, J = 5.5 Hz), 9.26 (s, 1H); ^{13}C NMR: δ 14.3 (CH_3), 23.2, 41.3 (both CH_2), 117.8, 123.9, 124.7, 127.2, 136.3, 145.6, 151.3 (all Ar-CH), 126.6, 128.8, 136.2, 144.7, 162.8 (all Ar-C); GC EI-MS: *m*/*z* (%) 222 (M^+, 4), 207 (21), 195 (11), 194 (100). Anal. Calcd. for $C_{15}H_{14}N_2$: C, 81.08; H, 6.30; N, 12.61. Found: C, 81.03; H, 6.30; N, 12.65.

2-Phenyl-1,8-phenanthroline (3d). Light brown needles (PE-EtOAc), 0.154 g (60%), mp 93–95°C; IR: 1625, 1601, 1588, 1555, 1439, 1382, 1216, 1037, 1022, 854, 757 cm^{-1}; ^1H NMR: δ 7.50 (dt, 1H, H-4′, J_1 = 7.5 Hz, J_2 = 1.0 Hz), 7.57 (t, 2H, H-3′,5′, J = 7.5 Hz), 7.79 and 7.85 (d, each, 1H, H-5, and H-6, respectively, J = 9.0 Hz), 8.09 and 8.25 (d, each, 1H, H-3, and H-4, respectively, J = 8.5 Hz,), 8.32 (dd, 2H, H-2′,6′, J_1 = 7.5 Hz, J_2 = 1.5 Hz,), 8.85 and 9.16 (d, each, 1H, H-9, and H-10, respectively, J = 5.5 Hz), 9.29 (s, 1H, H-7); ^{13}C NMR: δ 118.0 (CH-10), 121.0 (CH-3), 125.5 (CH-6), 127.0 (CH-5), 127.3 (C-4a), 127.8 (CH-2′,6′), 129.0 (C-6a), 129.3 (CH-3′,5′), 130.0 (CH-4′), 136.5 (C-10a), 137.1 (CH-4), 139.4 (C-1′), 145.0 (C-10b), 145.9 (CH-9), 151.4 (CH-7), 156.7 (C-2); GC EI-MS: *m*/*z* (%) 256 (M^+, 100), 255 (20), 229 (19), 228 (14). Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.37; H, 4.68; N, 10.93. Found: C, 84.30; H, 4.72; N, 10.98.

2-(4′-Nitrophenyl)-1,8-phenanthroline (3f). Yellow needles (PE-EtOAc), 0.174 g (58%), mp 255–256°C (dec.); IR: 1600, 1587, 1556, 1512, 1348, 1108, 1030, 850, 730 cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.10 and 8.15 (d, each, 1H, J = 9.0 Hz), 8.43 (d, 2H, J = 9.0 Hz), 8.58 and 8.69 (d, each, 1H, J = 8.5 Hz), 8.73 (d, 2H, J = 9.0 Hz), 8.89 and 9.10 (d, each, 1H, J = 5.5 Hz), 9.44 (s, 1H); ^{13}C NMR: could not be recorded because of its poor solubility in DMSO-d_6; GC EI-MS: *m*/*z* (%) 301 (M^+, 84), 299 (34), 271 (100), 255 (51), 243 (28), 229 (24), 227 (26). Anal. Calcd. for $C_{18}H_{11}N_3O_2$: C, 71.76; H, 3.65; N, 13.95. Found: C, 71.70; H, 3.63; N, 13.99.

2-(2′-Methoxyphenyl)-1,8-phenanthroline (3g). Cream-colored needles (PE–DCM), 0.197 g (69%), mp 117–119°C (dec.); IR: 1600, 1586, 1553, 1491, 1439, 1258, 1119, 1016, 850, 738, 725 cm^{-1}; ^1H NMR: δ 3.92 (s, 3H, OCH_3), 7.07 (d, 1H, J = 8.5 Hz), 7.19 (dt, 1H, J_1 = 7.5 Hz, J_2 = 1.0 Hz), 7.46 (dt, 1H, J_1 = 7.5 Hz, J_2 = 2.0 Hz), 7.82 and 7.86 (d, each, 1H, J = 9.0 Hz), 8.16 (dd, 1H, J_1 = 7.5 Hz, J_2 = 2.0 Hz), 8.20 and 8.25 (d, each, 1H, J = 8.5 Hz,), 8.82 and 9.13 (d each, 1H, J = 5.5 Hz,), 9.29 (s, 1H); ^{13}C NMR: δ 56.0

(OCH_3), 112.0, 118.0, 121.7, 125.4, 126.0, 127.18, 131.0, 132.3, 135.6, 145.7, 151.3 (all Ar-CH), 127.14, 128.8, 129.4, 136.6, 145.0, 156.3, 157.9 (all Ar-C); GC EI-MS: *m/z* (%) 286 (M^+, 100), 285 (80), 258 (14), 257 (58), 256 (30), 255 (32), 229 (23), 228 (24), 181 (81). Anal. Calcd. for $C_{19}H_{14}N_2O$: C, 79.72; H, 4.89; N, 9.79. Found: C, 79.77; H, 4.91; N, 9.76.

2-(4′-Methoxyphenyl)-1,8-phenanthroline (3h). Light brown globules (PE–DCM), 0.216 g (76%), mp 100–101°C; IR: 1594, 1552, 1499, 1253, 1177, 1019, 837, 785 cm^{-1}; ^1H NMR: δ 3.83 (s, 3H, OCH_3), 7.0 (dd, 2H, J_1 = 7.0 Hz, J_2 = 2.0 Hz,), 7.69, 7.74, 7.95 and 8.12 (d, each, 1H, J = 8.5 Hz), 8.2 (dd, 2H, J_1 = 7.0 Hz, J_2 = 2.0 Hz,), 8.76 (d, 1H, J = 5.0 Hz,), 9.06 (d, 1H, J = 5.5 Hz), 9.21 (s, 1H); ^{13}C NMR: δ 55.8 (OCH_3), 114.7 (2×), 118.0, 120.5, 125.1, 127.1, 129.2 (2×), 137.0, 145.5, 151.3 (all Ar-CH), 132.0, 136.5, 144.9, 156.4, 161.5 (all Ar-C); GC EI-MS: *m/z* (%) 286 (M^+, 100), 271 (30), 243 (38), 227 (17). Anal. Calcd. for $C_{19}H_{14}N_2O$: C, 79.72; H, 4.89; N, 9.79. Found: C, 79.69; H, 4.87; N, 9.81.

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