Long-Chain Alkyl-Substituted 1,10-Phenanthrolines as Surfactant Ligands for Transition-Metal Ions. 1. Synthesis of 4- and 4,7-*n*-Undecyl-Substituted 1,10-Phenanthrolines

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A convenient synthesis for 4- and 7-*n*-undecyl-1,10-phenanthrolines, based on a modified Doebner–von Miller reaction, is described for the following 1,10-phenanthrolines: 4-*n*-undecyl, 4,7-di-*n*-undecyl, 2-methyl-4-*n*-undecyl, 2,9-dimethyl-4-*n*-undecyl, and 2-methyl-7-*n*-undecyl.

Reseach conducted in our laboratory, centered around the reactivity of metal complexes supported in micellar or microemulsion solutions, has led us to investigate the synthesis of some substituted 1,10-phenanthroline ligands. Our goal in the present synthesis was to prepare 1,10-phenanthrolines containing long-chain aliphatic groups, such that, when coordinated with an appropriate metal ion, the complex would possess amphiphilic character, i.e., exhibit surface activity. Reports of the synthesis and characterization of similar surface-active metal complexes, based on substituted 2,2′-bipyridine ligands, have appeared in the literature (*1*), but the methods described have been tedious and result in low yields. We felt that analogous complexes could be obtained from substituted 1,10-phenanthrolines which not only would be easier to synthesize but also would allow a wider range of substituents to be built into the ligand.

The synthesis of substituted 1,10-phenanthrolines has, in the majority of cases, been accomplished by methods involving modifications of the Skraup reaction (*2–9*) or the Conrad–Limpach synthesis (*8*, *9*).

We have prepared several 4- and 7-*n*-undecyl-substituted 1,10-phenanthrolines (Table I) in good yield by a procedure based on a modified Doebner–von Miller-type reaction, described for the synthesis of 4-methylquinolines by Campbell and Schaffner (*10*). The method is attractive in that mild conditions and easily prepared starting materials are used.

The procedure consists of treating a 8-aminoquinoline or *o*-phenylenediamine in warm (65 °C) ethanol with an appropriate α,β-unsaturated ketone in the presence of a mild oxidizing agent, hydrochloric acid, and zinc chloride to give the substituted 1,10-phenanthroline in yields ranging from 17 to 52% (Scheme II, Figure 1). Campbell and Schaffner obtained the highest yields of lepidine when ferric chloride was used as the oxidizing agent (*10*). We chose to use sodium *m*-nitrobenzenesulfonate for the 1,10-phenanthroline synthesis, however, to avoid complications arising from complexation of the product as depicted in Scheme III of Figure 1.

The Skraup reaction (Scheme I, Figure 1) has commonly been used for 1,10-phenanthroline syntheses with varying degrees of success (*2*, *3*, *5–9*) and, in fact, gave us reasonable yields of 5-methyl-1,10-phenanthroline from 3,4-diaminotoluene and glycerol. This procedure, however, proved unsatisfactory for the preparation of the other 1,10-phenanthrolines described here, as workup of the reaction mixture gave only starting amine and tars. The failure of the Skraup reaction to give the desired phenanthroline is likely due to the low solubility of the high molecular weight ketone in sulfuric acid. This, coupled with the high heat/acidity conditions present, results in the preferential polymerization and decomposition of the unsaturated ketone, a problem often encountered in Skraup procedures. The modified Doebner–von Miller reaction described here is advantageous in that very little, if any, tar formation was encountered, providing a clean and straightforward workup.

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Experimental Section

Reagents. All reagents and solvents were obtained from commercial sources and were used without further purification, with the exception of the following. Chromium trioxide was dried at 110 °C for 24 h and stored in an evacuated desiccator over phosphorous pentoxide before use. Reagent-grade pyridine and methylene chloride were stored over 4-Å molecular sieves. Anhydrous diethyl ether and reagent-grade tetrahydrofuran (THF) were stored over metallic sodium, with the THF being distilled from potassium immediately before use.

Analysis. Proton nuclear magnetic resonance spectra were recorded on either a Varian T-60, 60-MHz or Varian EM-390, 90-MHz NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 599B infrared spectrophotometer. Microanalyses of the 1,10-phenanthrolines were performed by Atlantic Microlab, Inc., Atlanta, GA, and were submitted for review.

1-Tetradecen-3-ol. Vinyl bromide (36.4 g, 0.34 mol) was slowly added to a magnetically stirred suspension of magnesium turnings (7.24 g, 0.300 mol) in 100 mL of dry THF containing a small crystal of iodine. Once the addition of the vinyl bromide was complete, the reaction mixture was refluxed until the magnesium had dissolved (ca. 1.5 h). The resulting vinyl magnesium bromide solution was cooled to 0 °C, and dodecylaldehyde (36.8 g 0.200 mol) added over 1 h. The mixture was allowed to warm to room temperature overnight with stirring and was then quenched by pouring into 200 mL of 10% hydrochloric acid. This was extracted with three 100-mL portions of diethyl ether which were then combined, washed with 5% sodium bicarbonate solution, then with saturated brine, and dried over anhydrous magnesium sulfate. Removal of the solvent at reduced pressure yielded 38.2 g (90.0% yield) of crude 1-tetradecen-3-ol: NMR (60 MHz, $CDCl_3$) δ 5.8 (m, 1 H), 5.25 (d, J = 5 Hz, 1 H), 5.0 (m, 1 H), 4.08 (d, J = 3 Hz, 1 H), 2.65 (br s, 1 H), 1.25 (s, 20 H), 0.90 (t, J = 2.5 Hz, 3 H); IR (neat on NaCl) 3350s, 3080w, 2920s, 2850s, 1640w, 1465s, 1375w, 1055w, 985s, 915s, 715w cm^{-1}.

1-Tetradecen-3-one. The crude 1-tetradecen-3-ol (ca. 0.18 mol) was oxidized to the corresponding ketone with a chromium trioxide–pyridine complex in methylene chloride by using the procedure described by Ratcliffe and Rodehorst (*11*). Distillation of the crude product at 0.5 mmHg (97–105 °C) afforded 28.2 g (62% yield based on aldehyde) of a colorless oil: NMR (90 MHz, $CDCl_3$) δ 6.31 (m, 2 H), 5.8 (dd, J = 3 Hz, J' = 1 Hz, 1 H), 2.59 (t, J = 2.5 Hz, 2 H), 1.63 (t, J = 2.5 Hz, 2 H), 1.3 (s, 16 H), 0.89 (t, J = 2 Hz, 3 H); IR (neat on NaCl) 3085w, 2915s, 2845s, 1685, 1615s, 1462s, 1395s, 1375w, 1190w, 1080w, 985m, 958m, 915w, 718w cm^{-1}.

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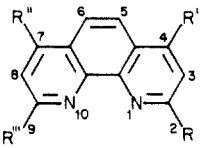
Table I. 1,10-Phenanthrolines



compd	R	R′	R″	R‴	1st component	ketone	yield, %	mp, °C
I	H	n-$C_{11}H_{23}$	H	H	8-aminoquinoline	1-tetradecen-3-one	44	52–54
IIa	CH_3	n-$C_{11}H_{23}$	H	H	8-aminoquinoline	2-pentadecen-4-one	52	88–90
IIb	CH_3	n-$C_{11}H_{23}$	H	H	8-aminoquinoline	1-pentadecen-4-one	48	88–90
III	CH_3	n-$C_{11}H_{23}$	H	CH_3	8-aminoquinaldine	1-pentadecen-4-one	45	48–50
IV	CH_3	H	n-$C_{11}H_{23}$	H	8-aminoquinaldine	1-tetradecen-3-one	44	40–42
V	H	n-$C_{11}H_{23}$	n-$C_{11}H_{23}$	H	o-phenylenediamine	1-tetradecen-3-one	17	66–68

Table II. ^{1}H NMR and Infrared Data for 1,10-Phenanthrolines (I-V)

compd	NMR (90 MHz, $CDCl_3$), δ	IR (neat melt on NaCl), cm^{-1}
I	9.34 (dd, J = 1.5 Hz, J' = 0.5 Hz, 1 H), 9.22 (d, J = 1.5 Hz, 1 H), 8.35 (dd, J = 2.5 Hz, J' = 0.5 Hz, 1 H), 8.03 (dd, J = 8 Hz, J' = 3 Hz, 2 H), 7.73 (d, J = 1.5 Hz, 1 H), 7.65 (d, J = 1.5 Hz, 1 H), 7.54 (d, J = 1.5 Hz, 1 H), 3.19 (t, J = 2.5 Hz, 2 H), 1.83 (t, J = 2.5 Hz, 2 H), 1.30 (s, 16 H), 0.89 (t, J = 2 Hz, 3 H)	3010w, 2910s, 2840s, 1615s, 1580s, 1555m, 1505s, 1460s, 1415s, 1375m, 835s, 775m, 730s, 630w
II	9.31 (dd, J = 1.5 Hz, J' = 0.5 Hz, 1 H), 8.28 (dd, J = 2.5 Hz, J' = 0.5 Hz, 1 H), 7.94 (dd, J = 9 Hz, J' = 3 Hz, 2 H), 7.69 (d, J = 1.5 Hz, 1 H), 7.60 (d, J = 1.5 Hz, 1 H), 7.42 (s, 1 H), 3.12 (t, J = 2.5 Hz, 2 H), 2.95 (s, 3 H), 1.79 (t, J = 2.5 Hz, 2 H), 1.30 (s, 16 H), 0.88 (t, J = 2 Hz, 3 H)	3010m, 2940w, 2910s, 2830s, 2000w, 1610s, 1580s, 1545m, 1485s, 1458s, 1420s, 1385m, 1370m, 1185w, 1140m, 1105m, 1040m, 950m, 880m, 850s, 835s, 785m, 760m, 720s, 640w, 610w
III	8.17 (d, J = 2.5 Hz, 1 H), 7.88 (dd, J = 9 Hz, J' = 3 Hz, 2 H), 7.52 (d, J = 9 Hz, J' = 3 Hz, 2 H), 7.52 (d, J = 2.5 Hz, 1 H), 7.40 (s, 1 H), 3.1 (t, J = 2.5 Hz, 2 H), 2.97 (d, J = 1 Hz, 6 H), 1.80 (t, J = 2.5 Hz, 2 H), 1.31 (s, 16 H), 0.9 (t, J = 2 Hz, 3 H)	3380m, 3020w, 2910s, 2840s, 1610s, 1580s, 1545m, 1490s, 1460m, 1370m, 1185m, 1150m, 1100m, 1030m, 875m, 840s, 730s, 640w
IV	9.20 (d, J = 1.5 Hz, 1 H), 8.19 (d, J = 2.5 Hz, 1 H), 7.91 (dd, J = 7.5 Hz, J' = 3 Hz, 2 H), 7.53 (d, J = 3 Hz, 1 H), 7.49 (d, J = 1.5 Hz, 1 H), 3.15 (t, J = 2.5 Hz, 2 H), 2.99 (s, 3 H), 1.8 (t, J = 2.5 Hz, 2 H), 1.3 (s, 16 H), 0.89 (t, J = 2 Hz, 3 H)	3020w, 2910s, 2840s, 1610s, 1590m, 1575s, 1550m, 1495s, 1460s, 1360m, 1240w, 1220w, 1130w, 875m, 840s, 730m, 705w
V	9.18 (d, J = 1.5 Hz, 2 H), 8.14 (s, 2 H), 7.51 (d, J = 1.5 Hz, 2 H), 3.15 (t, J = 2.5 Hz, 4 H), 1.8 (t, J = 2.5 Hz, 4 H), 1.3 (s, 32 H), 0.87 (t, J = 2 Hz, 6 H)	3020w, 2920s, 2845s, 1615m, 1575m, 1560m, 1510s, 1465s, 1415s, 1385m, 1370m, 1300w, 1220m, 1170m, 880m, 830s, 735m, 715m, 615m

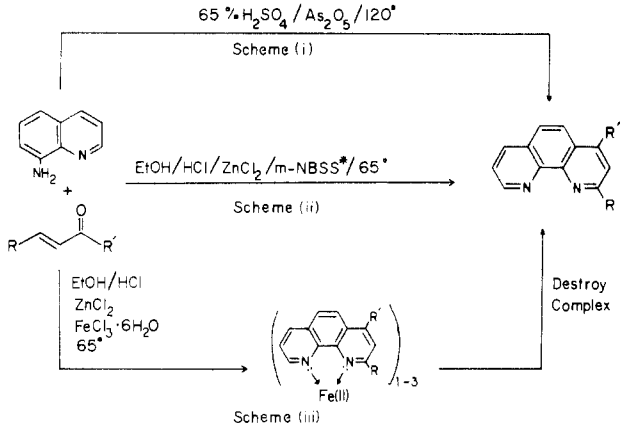


Figure 1. Reaction schemes for synthesis of a substituted 1,10-phenanthroline. See text for explanation of schemes. NBSS* = sodium *m*-nitrobenzenesulfonate.

1-Pentadecen-4-ol. This compound was prepared by allowing dodecylaldehyde (83 g, 0.45 mol) to react with allyl magnesium bromide (72.5 g, 0.5 mol), according to the procedure of Henze et al (*12*). The crude product (89 g, 87.4% yield) was collected as a pale yellow oil: NMR (90 MHz, $CDCl_3$) δ 5.90 (m, 1 H), 5.15 (d, J = 5 Hz, 2 H), 3.68 (br s, 1 H), 2.5 (br s, 1 H), 2.23 (m, 2 H), 1.3 (s, 20 H), 0.89 (t, J = 2 Hz, 3 H); IR (neat on NaCl) 3370s, 3070m, 2910s, 2845s, 1635m, 1460s, 1375m, 1345w, 1115s, 1070m, 1020m, 990m, 905s, 715m cm^{-1}.

1-Pentadecen-4-one. The crude 1-pentadecen-4-ol (ca. 0.4 mol) was oxidized by the procedure of Ratcliffe and Rodehorst (*12*). Distillation of the crude ketone yielded 52.4 g (58% yield based on aldehyde) of a colorless oil boiling from 108 to 110 °C at 0.45 mmHg: NMR (90 MHz, $CDCl_3$) δ 6.0 (m, 1 H), 5.24 (s, 1 H), 5.10 (d, J = 2.5 Hz, 1 H) 3.14 (d, J = 2.5 Hz, 2 H), 2.42 (t, J = 2.5 Hz, 2 H), 1.6 (t, J = 2.5 Hz, 2 H), 1.3 (s, 16 H), 0.88 (t, J = 2 Hz, 3 H); IR (neat on NaCl) 3070w, 2910s, 2840s, 1715s, 1635m, 1550m, 1460s, 1400w, 1370m, 985m, 910s, 715m cm^{-1}.

2-Pentadecen-4-one. Crude 1-pentadecen-4-ol (ca. 0.2 mol) was oxidized by a Jones-type method as described by Meinwald et al. (*13*). Distillation gave 12 g (27% yield based on aldehyde) of a colorless oil, which was collected from 100 to 105 °C at 0.1 mmHg: NMR (90 MHz, $CDCl_3$) δ 6.92 (dq, J_d = 5.25 Hz, J_q = 2.25 Hz, 1 H), 6.18 (dd, J = 5.25 Hz, J' = 0.5 Hz, 1 H), 2.54 (t, J = 2.5 Hz, 2 H), 1.89 (dd, J = 2.25 Hz, J' = 0.5 Hz, 3 H), 1.6 (t, J = 2.5 Hz, 2 H), 1.3 (s, 16 H), 0.88 (t, J = 2 Hz, 3 H); IR (neat on NaCl) 3025w, 2915s, 2840s, 1680s, 1628s, 1450s, 1405w, 1370s, 1280m, 1188m, 1130w, 1050w, 965s, 935w, 715m cm^{-1}.

Oxidation of ca. 0.4 mol of crude 1-pentadecen-4-ol with pyridinium chlorochromate (PCC), after the method of Corey and Suggs (*14*), provided a convenient route to the two isomeric ketones. Vacuum distillation of the crude oil obtained by this procedure afforded 47.7 g (50% yield based on aldehyde) of a mixture of both the α,β and β,γ unsaturated pentadecen-4-ones, in roughly equal proportions.

8-Aminoquinoline. 8-Nitroquinoline (43.5 g, 0.25 mol) was dissolved in 300 mL of 95% ethanol and heated to reflux with stirring. A 0.32 M solution of ammonium sulfide in ethanol (230 mL, 0.74 mol) was added to the refluxing reaction mixture over 1 h, and reflux continued an additional 2 h. The solution was transferred to a 2-L beaker, and 200 mL of 6 N hydrochloric acid was added cautiously. The resulting mixture was filtered, cooled, and made basic with concentrated ammonium hydroxide, and the crude product collected after standing ice-cold

overnight. Distillation at 0.2 mmHg gave 29.2 g (81% yield) of a pale yellow solid (mp, 66–67 °C): NMR (90 MHz, $CDCl_3$) δ 8.87 (dd, J = 1.5 Hz, J' = 0.5 Hz, 1 H) 8.15 (dd, J = 2.5 Hz, J' = 0.5 Hz, 1 H), 7.32 (m, 3 H), 6.98 (dd, J = 2.5 Hz, J' = 0.5 Hz, 1 H), 5.05 (br s, 2 H); IR (KBr pellet) 3450s, 3350s, 3050w, 3015w, 3000w, 1610s, 1595m, 1560m, 1500s, 1465s, 1425m, 1365s, 1330s, 1125m, 1095m, 815s, 785s, 760s, 640m cm^{-1}.

2-Methyl-8-nitroquinoline (8-Nitroquinaldine). This compound was prepared from *o*-nitroaniline (0.4 mol) and crotonaldehyde (0.6 mol), under the conditions of the Yale modification of the Skraup reaction as described by Case (*8*). Crystallization of the product from benzene/petroleum ether gave 33.6 G (44.5% yield) of rust-colored crystals. A portion, recrystallized from dilute ethanol, gave light yellow–orange needles (mp, 135–137 °C): NMR (90 MHz, $CDCl_3$) δ 8.1 (m, 3 H), 7.55 (m, 2 H), 2.79 (s, 3 H); IR (KBr pellet) 3020w, 2950w, 2905w, 1620w, 1598s, 1520w, 1430w, 1370s, 1310s, 1245m, 1205m, 1139m, 900w, 860s, 830s, 790s, 760s, 720w, 695w, 650s cm^{-1}.

2-Methyl-8-aminoquinoline (8-Aminoquinaldine). This was prepared by ammonium sulfide reduction of 8-nitroquinaldine in a fashion identical with that described for the preparation of 8-aminoquinoline. Crystallization from dilute ethanol gave 12.8 g (45% yield) of light yellow needles (mp, 48–50 °C): NMR (90 MHz, $CDCl_3$) δ 8.01 (d, J = 3 Hz, 1 H), 7.25 (m, 3 H), 6.93 (dd, J, = 2.5 Hz, J' = 0.5, 1 H), 4.8 (br s, 2 H), 2.73 (s, 3 H); IR (neat melt on NaCl) 3450s, 3350s, 3020m, 2895m, 2830w, 1605m, 1580s, 1550m, 1490s, 1460s, 1365s, 1330s, 1310m, 1265m, 1230m, 1115m, 1065m, 1020m, 818s, 785s, 735s, 710w cm^{-1}.

General Procedure for 1,10-Phenanthroline Synthesis. To a magnetically stirred solution of 0.025 mol of either 8-aminoquinoline or 8-aminoquinaldine in 125 mL of 95% ethanol was added 0.5 g of anhydrous zinc chloride, 7.5 g (0.032 mol) of sodium *m*-nitrobenzene sulfonate, and 10 mL (0.12 mol) of concentrated hydrochloric acid. The mixture was heated to 65–70 °C, and 0.025 mol of the appropriate ketone dissolved in 25 mL of 95% ethanol was added over 1.5 h. Once the addition of the ketone was complete, the mixture was allowed to reflux overnight. The reaction was cooled, most of the alcohol removed under reduced pressure, and the residue taken up in 200 mL of concentrated ammonium hydroxide. This was extracted with two portions of methylene chloride, and the organic phases were combined and evaporated to a yellow–brown oil. The oil was taken up in a minimum of ethanol, 300 mL of 10% hydrochloric acid was added, and the mixture was allowed to stand ice-cold overnight. The crude phenanthroline hydrochloride was collected and dissolved in ethanol, and the crude base was precipitated by addition of concentrated ammonium hydroxide. After cooling, the product was collected and recrystallized from hexane as pale yellow or cream-colored needles.

In the case of 4,7-di-*n*-undecyl-1,10-phenanthroline (compound V), 2.8 g (0.025 mol) of *o*-phenylenediamine was used, along with 15 g (0.064 mol) of sodium *m*-nitrobenzene sulfonate, 1 g of zinc chloride, and 20 mL of concentrated hydrochloric acid. 1-Tetradecen-3-one (10 g, 0.048 mol) was added over 3 h at 60 °C, the rest of the reaction proceeding as before. The final product was recrystallized from acetone.

The phenanthrolines crystallized as the hydrated ligands initially, but the anhydrous compounds were readily obtained by drying under vacuum over phosphorous pentoxide for 10–12 h. Compound III (2,9-dimethyl-4-*n*-undecyl-1,10-phenanthroline) gave only a partially hydrated ligand of formula $C_{25}H_{34}N_2 \cdot 1/4H_2O$ after repeated drying over phosphorus pentoxide at 10^{-2} mmHg. The results of the phenanthroline syntheses appear in Tables I and II.

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