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SHORT COMMUNICATIONS

$LnCl_3 \cdot 6H_2O$ Crystal Hydrates as Highly Effective Catalysts in the Synthesis of Alkyl-Substituted Quinolines and Phenanthrolines

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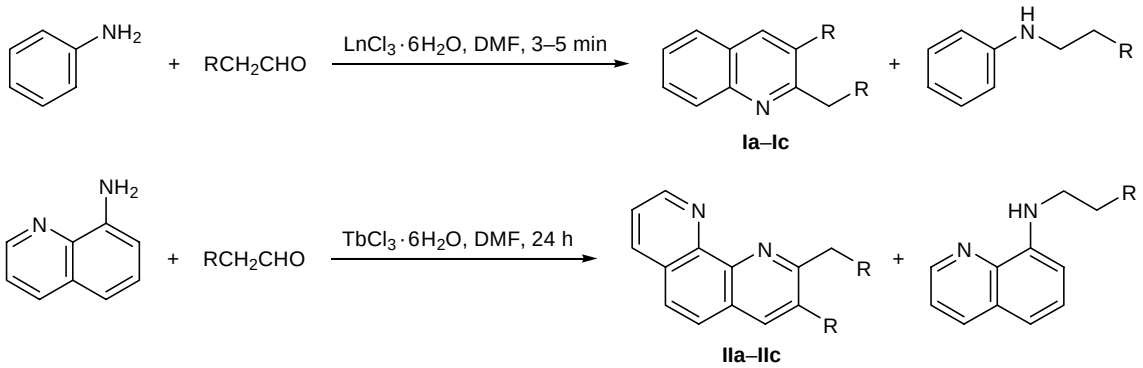
The three-component system $LnCl_3$–Ph_3P–DMF is the most effective catalyst for the synthesis of alkyl-substituted quinolines, naphthyridines, and phenanthrolines by condensation of aliphatic aldehydes with aniline and 4- or 8-aminoquinolines (high pressure, 100°C, 6 h) [1]. Reactions of aldehydes with substituted anilines and cyclopentadiene in acetonitrile [2] or with alkylamine hydrochlorides in water [3], catalyzed by lanthanide trifluoromethanesulfonate complexes $Ln(OTf)_3$, allow substituted tetrahydroquinolines, pyridines, and dihydropyridines to be obtained in high yield at room temperature in 24 h. There are no published data on the use of $Ln(OTf)_3$ in the synthesis of alkyl-substituted quinolines, naphthyridines, and phenanthrolines.

We have found that 2,3-dialkylquinolines **Ia**–**Ic** and 2,3-dialkyl-1,10-phenanthrolines **IIa**–**IIc** are formed in high yield at 20°C in polar solvents, including ecologically safe ones (EtOH, DMSO), in the presence of $LnCl_3 \cdot 6H_2O$ crystal hydrates **III** as catalyst. The reactions occur under atmospheric pressure and are characterized by complete conversion of the initial reactants. The reactions with aniline take 3–5 min, while the synthesis of phenanthrolines **II** required considerably longer time (20–24 h). The nature of the carbonyl component weakly affects the selectivity and yield. Using the reaction of aniline with butyraldehyde as an example, we examined the effect of the lanthanide and solvent natures on the yield and obtained the following series:

Tb (95%) ≈ Ho (94) > Gd (92) > Nd (90) > Pr (88) > Eu (66) > Ce (61);

DMF (95) > DMSO (93) ≈ EtOH (92) > toluene (67) > hexane (61).

The catalytic activity increases in parallel with the ability of lanthanide ion to form complexes with electron-donor ligands. Presumably, the lower catalytic



R = Et (**a**), Pr (**b**), Bu (**c**).

activity of europium is explained by the known [4] ability of Eu(III) to undergo reduction to Eu(II) which has a lower coordination number. The catalysis in nonpolar solvents is less effective, for the reaction system is heterogeneous.

Crystal hydrates **III** are more advantageous than the known catalysts [1–3] due to their ready accessibility (they are available as low-cost commercial products). In addition, crystal hydrates **III** are effective in catalytic amounts (0.2 mol %), whereas about 5 mol % of $Ln(OTf)_3$ is necessary to ensure comparable efficiency.

2,3-Dialkylquinolines Ia–Ic (*general procedure*). Aniline, 1.8 ml (20 mmol), and the corresponding aldehyde, 44 mmol, were added in succession to a solution of 0.4 mmol of $LnCl_3 \cdot 6H_2O$ in 7 ml of DMF. After 5–10 min, the mixture was extracted with diethyl ether (3×50 ml), the extracts were combined and dried over $MgSO_4$, the solvent was distilled off, and the residue was subjected to fractional distillation under reduced pressure.

3-Ethyl-2-propylquinoline (Ia). Yield 95%. Oily liquid, bp 118°C (1 mm). ^{1}H NMR spectrum, δ, ppm: 1.08 t (3H, CH_3), 1.23 t (3H, CH_3), 1.71 m (2H, CH_2), 2.68 q (2H, CH_2), 2.85 t (2H, CH_2), 7.3–8.1 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.91 q (C^{13}), 14.0 q (C^{15}), 23.4 t (C^{12}), 24.7 t (C^{14}), 37.22 t (C^{11}), 125.05 s (C^{10}), 125.15 d (C^8), 126.48 d (C^6), 127.0 d (C^5), 128.1 d (C^7), 133.2 d (C^4), 134.7 s (C^3), 146.07 s (C^9), 161.33 s (C^2). Found, %: C 84.64; H 8.35; N 7.01. $C_{14}H_{17}N$. Calculated, %: C 84.42; H 8.54; N 7.04.

2-Butyl-3-propylquinoline (Ib). Yield 92%. Oily liquid, bp 143°C (1 mm). ^{1}H NMR spectrum, δ, ppm: 1.1 t (3H, CH_3), 1.25 t (3H, CH_3), 1.68 m (2H, CH_2), 1.73 m (2H, CH_2), 1.82 t (2H, CH_2), 2.71 q (2H, CH_2), 7.28–8.07 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.80 q (C^{14}), 13.90 q (C^{17}), 22.80 t (C^{13}), 23.20 t (C^{16}), 31.10 t (C^{12}), 33.70 t (C^{15}), 35.00 t (C^{11}), 125.10 d (C^8), 126.20 d (C^6), 126.80 s (C^{10}), 128.10 d (C^5), 128.15 d (C^7), 133.10 d (C^4), 134.20 s (C^3), 145.80 s (C^9), 161.10 s (C^2). Found, %: C 84.35; H 9.63; N 6.02. $C_{16}H_{21}N$. Calculated, %: C 84.58; H 9.25; N 6.17.

3-Butyl-2-pentylquinoline (Ic). Yield 90%. Oily liquid, bp 156°C (1 mm). ^{1}H NMR spectrum, δ, ppm: 1.12 t (3H, CH_3), 1.27 t (3H, CH_3), 1.78 m (2H, CH_2), 1.86 m (2H, CH_2), 1.86 m (2H, CH_2), 1.97 m (2H, CH_2), 2.13 m (2H, CH_2), 2.38 m (2H, CH_2), 2.83 q (2H, CH_2), 2.97 t (2H, CH_2), 7.3–8.12 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.02 q (C^{15}), 14.07 q (C^{19}), 22.55 t (C^{14}), 22.72 t (C^{18}), 28.39 t (C^{13}), 29.76 t (C^{17}), 31.98 t (C^{12}), 32.44 t (C^{16}), 35.70 t (C^{11}), 123.70 d (C^8), 124.70 d (C^6), 125.10 s (C^{10}), 126.80 d (C^5), 128.10 d (C^7), 132.80 d (C^4), 132.70 s (C^3), 141.50 s (C^9), 160.70 s (C^2). Found, %: C 85.5; H 9.3; N 5.2. $C_{18}H_{25}N$. Calculated, %: C 84.70; H 9.80; N 5.50.

2,3-Dialkyl-1,10-phenanthrolines IIa–IIc (*general procedure*). 8-Aminoquinoline, 2.88 g (20 mmol), and the corresponding aldehyde, 44 mmol, were added in succession to a solution of 0.4 mmol of $TbCl_3 \cdot 6H_2O$ in 7 ml of DMF. The mixture was stirred for 24 h at 20°C and extracted with diethyl ether (3×50 ml), the extracts were combined and dried over $MgSO_4$, the solvent was distilled off, and the residue was purified by column chromatography on Al_2O_3 using hexane–diethyl ether (1:10) as eluent.

3-Ethyl-2-propyl-1,10-phenanthroline (IIa). Yield 65%. Oily liquid, bp 208–210°C (1 mm). ^{1}H NMR spectrum, δ, ppm: 1.08 t (3H, CH_3), 1.35 t (3H, CH_3), 1.95 m (2H, CH_2), 2.91 q (2H, CH_2), 3.15 t (2H, CH_2), 7.67–9.20 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.48 q (C^{17}), 14.48 q (C^{19}), 23.62 t (C^{16}), 25.18 t (C^{18}), 38.27 t (C^{15}), 122.18 d (C^5), 125.35 d (C^6), 126.3 d (C^4), 127.52 s (C^{11}), 128.34 s (C^{13}), 134.45 d (C^8), 135.88 d (C^7), 143.50 s (C^3), 146.13 s (C^{12}), 150.15 d (C^9), 150.43 s (C^{14}), 162.23 s (C^2). Found, %: C 81.3; H 7.9; N 10.8. $C_{17}H_{18}N_2$. Calculated, %: C 81.6; H 7.2; N 11.2.

2-Butyl-3-propyl-1,10-phenanthroline (IIb). Yield 62%. Oily liquid, bp 214–216°C (1 mm). ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3), 1.23 t (3H, CH_3), 1.50–2.10 m (6H, CH_2), 2.91– 3.30 m (4H, CH_2), 7.50–9.21 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.15 q (C^{18}), 14.35 q (C^{21}), 23.31 t (C^{17}), 24.30 t (C^{20}), 28.61 t (C^{16}), 31,7 t (C^{19}), 34.60 t (C^{15}), 122.9 d (C^5), 125.96 d (C^6), 126.44 d (C^4), 127.42 s (C^{11}), 128.21 s (C^{13}), 128.77 d (C^8), 131.86 d (C^7), 132.25 s (C^3), 135.91 s (C^{12}), 142.57 s (C^{14}), 150.01 d (C^9), 160.84 s (C^2). Found, %: C 81.7; H 8.1; N 10.2. $C_{19}H_{22}N_2$. Calculated, %: C 82.0; H 7.9; N 10.1.

3-Butyl-2-pentyl-1,10-phenanthroline (IIc). Oily liquid, bp 198–210°C (1 mm). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3), 0.98 t (3H, CH_3), 1.40–1.90 m (10H, CH_2), 2.85 t (2H, CH_2), 3.20 t (2H, CH_2), 7.50–9.20 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.01 q (C^{19}), 14.18 q (C^{23}), 22.59 t (C^{18}), 22.88 t (C^{22}), 30.80 t (C^{17}), 32.06 t (C^{21}), 32.38 t (C^{16}), 32.82 t

(C^{20}), 36.49 t (C^{15}), 122.21 d (C^5), 125.36 d (C^6), 126.26 d (C^4), 127.41 s (C^{11}), 128.33 s (C^{13}), 135.38 d (C^8), 135.90 d (C^7), 135.99 s (C^3), 143.99 s (C^{12}), 146.18 s (C^{14}), 150.17 d (C^9), 162.56 s (C^2). Found, %: C 82.8; H 8.2; N 9.0. $C_{21}H_{26}N_2$. Calculated, %: C 82.4; H 8.5; N 9.1.

The elemental compositions were determined on a Carlo Erba 106 analyzer. The ^1H and ^{13}C NMR spectra were recorded on a Jeol FX 90Q spectrometer using $CDCl_3$ as solvent and TMS as internal reference.

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REFERENCES

1. Selimov, F.A., Ptashko, O.A., and Dzhemilev, U.M., *Sintez piridinovykh osnovanii pod deistviem metallokompleksnykh katalizatorov* (Synthesis of Pyridine Bases Using Metal-Complex Catalysts), Moscow: Khimiya, 2003.
2. Powell, D.A. and Batey, R.A., *Tetrahedron Lett.*, 2003, vol. 46, p. 7569.
3. Li-Bing Yu, Depu Chen, Jun Li, Ramires, J., and Wang, P.G., *J. Org. Chem.*, 1997, vol. 62, p. 208.
4. Serebrennikov, V.V. and Alekseenko, L.A., *Kurs khimii redkozemel'nykh elementov* (Lectures on the Chemistry of Rare-Earth Elements), Tomsk: Tomsk. Univ., 1963.