

SHORT
COMMUNICATIONS**Catalytic Activity of Iron(III), Aluminum(III),
Cobalt(II), and Magnesium(II) Chloride Crystal Hydrates
in the Condensation of Aniline with Butyraldehyde**

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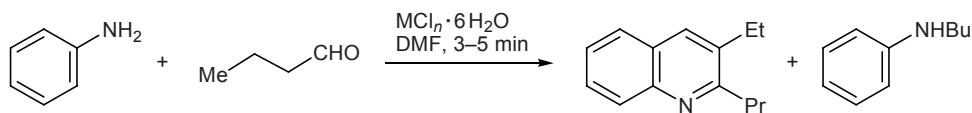
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Quinoline and its derivatives are used as starting compounds in the synthesis of cyanine dyes, as extractants, sorbents, and corrosion inhibitors [1]. Lanthanide chloride crystal hydrates $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ are known to be the most effective catalysts in the synthesis of alkyl-substituted quinolines via condensation of aniline with aliphatic aldehydes [2]. Unlike anhydrous lanthanide chlorides LnCl_3 and coordination compounds or salts of other metals $\{\text{RuCl}_2(\text{PPh}_3)_3, \text{RuCl}_3, \text{Ni}(\text{acac})_2 [1]\}$, lanthanide chloride crystal hydrates make it possible to synthesize alkylquinolines in high yield under mild conditions. The above series of metal compounds is strongly limited, for other, more accessible metal chloride crystal hydrates have not been tested so far for catalytic activity in the synthesis of quinolines. With the goal of optimizing methods for the preparation of quinoline derivatives via search for cheaper catalysts it was reasonable to test for catalytic activity a broader series of crystal hydrates which were not examined previously.

In the present work we studied the catalytic activity of a series of the most accessible and least expensive crystal hydrates ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and NaCl) in the condensation of aniline with butyraldehyde in DMF (EtOH) at $\sim 20^\circ\text{C}$, which leads to the formation of 3-ethyl-2-propylquinoline. The results showed the following catalytic

activity series of the examined crystal hydrates (yield, %): $\text{Fe} (94) > \text{Al} (89) > \text{Co} (55) > \text{Mg} (45) > \text{Na} (15)$. The catalytic efficiency increases in parallel with the known [3] complexing ability of metal ion toward electron-donating ligands (coordination numbers of Fe^{3+} , Al^{3+} , and Co^{2+} are equal to 6, 6, and 4, respectively). The yield of 3-ethyl-2-propylquinoline in the presence of sodium chloride (which does not form complexes) was almost the same as in the reaction performed in the absence of metal chloride. The best yield was obtained using the cheapest crystal hydrate, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst, and its catalytic activity was no less than that of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ which is known as the most active catalyst in the above condensation. The reaction starts even at 20°C (760 mm), is complete in a short time (3–5 min), and is accompanied by heat evolution (the mixture warms up to $\sim 70^\circ\text{C}$). In 1 h after the reaction completion, the originally homogeneous solution divided into two layers; the catalyst resides in the bottom (heavier) phase, and it can be readily separated as brownish solid. The catalyst can be reused; the yield of 3-ethyl-2-propylquinoline in the second cycle was 87%.

Thus we were the first to reveal high catalytic activity of one of the most accessible and cheapest crystal hydrate manufactured in Russia, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, in the condensation of aniline with butyraldehyde.

M = Fe(III), Al(III), Co(II), Mg(II); $n = 2-3$.

3-Ethyl-2-propylquinoline. The corresponding metal chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, or NaCl , 0.4 mmol, was dissolved in 7 ml of DMF (EtOH), and 1.8 ml (20 mmol) of aniline and 3.96 ml (44 mmol) of butyraldehyde were added in succession. 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. The boiling point, ^1H and ^{13}C NMR spectra, and elemental composition of the product were consistent with the structure of 3-ethyl-2-propylquinoline and previously reported data [2].

The ^1H and ^{13}C NMR spectra were recorded on a Jeol FX-90Q spectrometer using chloroform-*d* as

solvent and tetramethylsilane as internal reference. The elemental composition was determined on a Carlo Erba Model 106 analyzer.

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