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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of 2-Hydroxy-1-Naphthaldehyde under Conditions of Heterogeneous Catalysis

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Abstract—A procedure was developed for synthesis of 2-hydroxy-1-naphthaldehyde by Reimer–Tiemann fluorination of 2-naphthol under conditions of heterogeneous catalysis.

Aromatic *o*-hydroxy aldehydes readily enter cyclizations and are therefore important synthetic precursors of carbocyclic and heterocyclic compounds. For example, 2-hydroxy-1-naphthaldehyde **I** is widely used for preparing various luminophores, optical whiteners [1, 2], analytical reagents [3], and drugs.

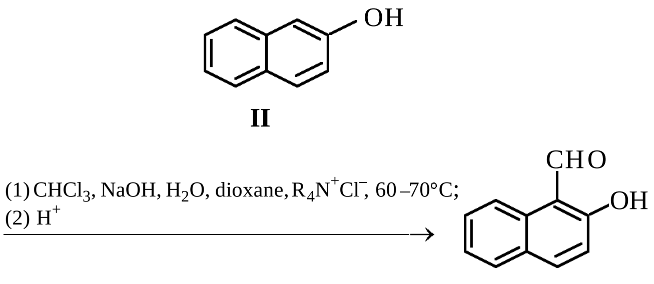
In synthesis and study of various benzocoumarin derivatives, a need arose for relatively large amounts of **I**. Published procedures for preparing **I** [4–7], despite high yields (up to 80%), are complicated by use of expensive and deficient reagents, which are often toxic.

The most acceptable route to **I**, free of the above drawbacks, is formylation of 2-naphthol **II** by the Reimer–Tiemann reaction; however, in the classical version of this procedure, the yields are as low as 38–48% [8], and isolation of a high-purity product is difficult, which makes this procedure unsuitable for large-scale syntheses.

To raise the yield and obtain high-purity product, we examined the possibility of formylation of **II** with chloroform in alkaline solution under conditions of heterogeneous catalysis [9]. Although the Reimer–Tiemann reaction usually does not require catalysts, it was shown in [10] that the use of tertiary ammonium salts for preparing salicylaldehyde from phenol increases the yield of the target product by more than a factor of 2.

Along with the low cost and availability of the starting compounds (naphthol **II**, chloroform, alkali), an advantage of the heterogeneous-catalytic synthesis in alkaline solution is the formylation at the *o*-position and the minimum extent of condensation of the forming aldehyde **I** with the initial naphthol **II**. The possibility of such a condensation in acid solutions with the formation of dibenzoxanthene derivatives and oligomeric substances contaminating the target product was noted in [11].

Aldehyde **I** was prepared by the scheme



II

I

It is well known that the reactive species in the Reimer–Tiemann reaciton is dichlorocarbene :CCl_2. The mechanism of dichlorocarbene generation under conditions of heterogeneous catalysis is also understood in detail [12]. The reaction scheme can be described as follows. At the phase boundary, chloroform is deprotonated to give trichloromethylide anion:

$$HCCl_{3(\text{org. phase})} + Na^+_{(\text{aq. phase})} + OH^-_{(\text{aq. phase})} \rightleftarrows CCl^-_{3(\text{interface})} + Na^+_{(\text{interface})} + H_2O. \qquad (1)$$

This is followed by exchange with the quaternary ammonium salt (2) and generation of carbene (3) (the reaction is reversible):

$$CCl^-_{3(\text{interface})} + [R_4N^+X^-]_{(\text{org. phase})} \rightleftarrows [R_4N^+CCl_3^-]_{(\text{org. phase})} + X^-_{(\text{aq. phase})}, \qquad (2)$$

$$[R_4N^+CCl_3^-]_{(\text{org. phase})} \rightleftarrows [R_4N^+Cl^-]_{(\text{org. phase})} + [CCl_2]_{(\text{org. phase})}. \qquad (3)$$

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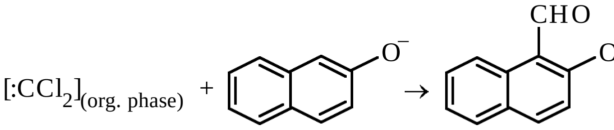
The carbene formed irreversibly reacts with the substrate:



(4)

The reaction was performed in a two-phase aqueous-organic system. The organic phase was 1,4-dioxane or a mixture of 1,4-dioxane with a branched alcohol in a ratio varying from 10 : 1 to 30 : 1. Branched alcohols were added to raise the solubility of sodium naphtholate in the organic phase. As catalysts we tested quaternary ammonium salts: tetrabutylammonium (TBAC), benzyltriethylammonium (TEBAC), and benzyltrimethylammonium (TMBAC) chlorides (0.1–0.4 mol %). Dichlorocarbene was generated from excess chloroform and 40% aqueous NaOH. The reaction was performed at 60–70°C.

The experimental results (see table) show that the Reimer–Tiemann formylation of naphthol **II** under conditions of heterogeneous catalysis gives the target product in a yield 1.5–2 times higher than that in the classical version of this reaction.

The best results were obtained with tetrabutylammonium chloride as phase-transfer catalyst; however, as seen from the table, with the yields the other catalysts are only slightly lower.

It should be noted that this procedure is very easy. Most of the impurities are removed in the stage of isolation of the hydroxy aldehyde sodium salt, so that the target product can be obtained 98% pure without vacuum distillation.

Heterogeneous-catalytic synthesis of hydroxy aldehyde **I** (65–70°C)

Catalyst, mol %	Organic phase,* ml	Yield, %
BuN^+Cl^-:		
0.4	*i*-BuOH, 5	78
0.1**	*i*-AmOH, 5	68**
0.2	*i*-BuOH, 5	73
0.3	*i*-PrOH, 15	76
TEBAC:		
0.1	*i*-BuOH, 5	71
0.2	*i*-PrOH, 15	73
0.4	*i*-AmOH, 10	77
TEMAC:		
0.1	*i*-BuOH, 5	70
0.2	*i*-BuOH, 5	74
0.4	*i*-BuOH, 5	78

* In all runs, the second component is dioxane (150 ml). ** At 68–72°C.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Tesla BS-587A spectrometer (100 MHz, internal reference TMS). The IR spectra were taken on a Specord M-80 spectrometer in the range 400–4000 cm^{-1}, using KBr pellets. The melting points were determined on a Boetius stage.

2-Hydroxy-1-naphthaldehyde I. A flask equipped with stirrer, thermometer, reflux condenser, and dropping funnel was charged with 144.2 g (1 mol) of naphthol **II** and 400 ml of 40% NaOH. The mixture was stirred for 0.5 h to obtain a homogeneous solution. Then the mixture was cooled to 65–70°C, and 1.15 g (0.004 mol) of a quaternary ammonium salt and 130 ml of a 30 : 1 mixture of 1,4-dioxane with a branched alcohol were added. This was followed by addition of chloroform (155.2 g, 1.3 mol) at a rate ensuring reaction temperature within 70°C. After adding the whole amount of chloroform, the mixture was stirred at 65–70°C for an additional 1 h and cooled to 20°C; 2-hydroxy-1-naphthaldehyde sodium salt was filtered off. The resulting crystalline product was washed successively with 1% NaOH and a 20 : 1 mixture of dioxane with 1% aqueous NaOH. The wet residue was transferred into a flask and stirred for 1 h with 300 ml of 10–15% aqueous HCl. The precipitate of aldehyde **I** was filtered off, washed with water to neutral reaction and negative reaction for chloride ions, and dried in a desiccator over $CaCl_2$. Yield 78%, mp 80–82°C, main substance content 98%.

The physicochemical and spectral characteristics of **I** are in agreement with reference data [8].

CONCLUSIONS

(1) 2-Naphthol is regioselectively formylated under conditions of the heterogeneous-catalytic version of the Reimer–Tiemann reaction to give 2-hydroxy-1-naphthaldehyde.

(2) This procedure allows preparation of a high-purity target product in 75% yield.

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