Russian Journal of Applied Chemistry, Vol. 75, No. 3, 2002, pp. 511–512. Translated from Zhurnal Prikladnoi Khimii, Vol. 75, No. 3, 2002, pp. 522–523.
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BRIEF COMMUNICATIONS

Phase-Transfer Catalysis in Synthesis of Oximes

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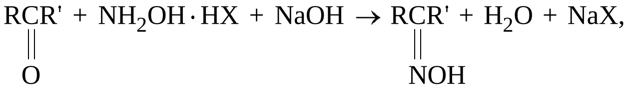
Received September 25, 2001

Abstract—Perfluorinated higher carboxylic acids were tested as phase-transfer catalysts in synthesis of oximes.

The known synthetic routes to oximes are based on reaction of a carbonyl compound with an aqueous solution of a hydroxylamine salt [1–3] in the presence of inorganic compounds, e.g., of NaOH:



$$\underset{\substack{\|\\ O}}{RCR'} + NH_2OH\cdot HX + NaOH \rightarrow \underset{\substack{\|\\ NOH}}{RCR'} + H_2O + NaX,$$

where R = Alk; R' = Alk, H, Ar, Ht; X is an inorganic anion.

Because carbonyl compounds, as a rule, are poorly soluble in water, the reaction is usually performed in aqueous alcohol. However, the reaction is slow (5–8 h) and does not go to completion even in the presence of excess hydroxylamine salt. The yield of the oxime based on the taken carbonyl compound usually does not exceed 80%.

To promote the reaction, various phase-transfer catalysts were tested without using an organic solvent. We found that the most effective phase-transfer catalysts for oximation are higher perfluorinated carboxylic acids exhibiting a high surface activity. Addition of these compounds (0.07–0.10 wt %) appreciably shortens the reaction time and allows preparation of oximes in high, sometimes almost quantitative yields. This can be illustrated by several examples.

Acetophenone oxime. (a) A 1-l reaction vessel equipped with a thermometer, a reflux condenser, a stirrer, and a dropping funnel was charged with a solution of 76.5 g (1.1 mol) of hydroxylamine hydrochloride in 200 ml of water and 120 g (1.0 mol) of acetophenone, and a 20% solution of 44 g (1.1 mol) of NaOH was added dropwise with stirring at 36°C until pH 7–8 was attained. The mixture was heated at 60–70°C for 5 h and then cooled to 0–3°C. The resulting crystalline precipitate was filtered off, washed with several portions of ice-cold water, and dried in a desiccator over $CaCl_2$ to constant weight; 100 g of acetophenone oxime was obtained, mp 57°C (published data [2, 3]: 57–58°C); yield 70%.

(b) The reaction was performed similarly to procedure (a) but in the presence of 0.61 g (1.7 mmol) of perfluoroenanthic acid with addition of a 20% NaOH solution at 60–70°C; the mixture was heated at this temperature for 3.5 h. Yield of acetophenone oxime 131.6 g (98%).

(c) The reaction was performed similarly to procedure (a) but in the presence of 0.61 g (2.3 mmol) of perfluorovaleric acid; time of heating at 60–70°C 3 h. Yield of acetophenone oxime 132.3 g (99%).

5-Methyl-3-hexanone oxime. A reaction vessel [the same as in procedure (a)] was charged with 57 g (0.8 mol) of 5-methyl-3-hexanone, 39 g (0.56 mol) of hydroxylamine hydrochloride, 100 ml of water, and 0.6 g (1.65 mmol) of perfluoroenanthic acid; 100 ml of 25% aqueous NaOH was added, keeping the temperature below 35°C, after which the mixture was heated to 67–68°C and kept at this temperature for 3 h. After cooling, the upper layer was separated, washed with three 20-ml portions of cold water, and distilled in a vacuum (10–12 mm Hg). A fraction boiling at 85–95°C was collected. Yield of 5-methyl-3-hexanone oxime 49.7 g (71%); n_D^{20} 1.4424 (published data [4]: n_D^{20} 1.4436).

Salicylaldoxime. Similarly to procedure (a), a 500-ml reactor was charged with 26 g (0.21 mol) of salicylaldehyde, 16 g (0.21 mol) of hydroxylamine hydrochloride, 40 ml of water, and 0.2 g (0.55 mol) of perfluoroenanthic acid; a solution of 9 g (0.225 mol) of NaOH in 30 ml of water was slowly added, after which the mixture was heated to 65–70°C and kept at this temperature for 3 h. After cooling to 5–10°C, the mixture was worked up similarly to procedure (a).

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Yield of salicylaldoxime 26 g (98%), mp 58°C (published data [5]: 57–59°C).

3-Thioxo-2-butanone oxime. Similarly to synthesis of salicylaldoxime, a reactor was charged with 25.2 g (0.247 mol) of 3-thioxo-2-butanone, a solution of 16 g (0.23 mol) of hydroxylamine hydrochloride in 210 ml of water, and 0.2 g (0.55 mol) of perfluoroenanthic acid, after which a solution of 9 g (0.225 mol) of NaOH in 30 ml of water was added dropwise at 30–35°C. The mixture was heated to 70°C and kept at this temperature for 3 h. After cooling, the mixture was worked up as described above. Yield of 3-thioxo-2-butanone oxime 20.8 g (74%); mp 105–106°C. The structure was confirmed by IR spectroscopy.

Thus, addition of perfluorinated carboxylic acids increases the yield of oximes, shortens the reaction time, and eliminates the necessity of using an organic solvent, which considerably simplifies the oximation process.

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