



Short communication

Cobalt/nitrophenolate-catalyzed selective conversion of aldoximes into nitriles or amides



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ARTICLE INFO

Article history:

Received 10 October 2014

Received in revised form 19 November 2014

Accepted 21 November 2014

Available online 22 November 2014

Keywords:

Cobalt

Amides

Nitriles

Homogeneous catalysis

Selective conversions

ABSTRACT

A novel cobalt/nitrophenolate complex has been synthesized, characterized and studied for their catalytic activities. Conversion of aldoximes to nitriles can be performed via in situ conditions from cobalt(II) acetate and 2,4-dinitrophenol. The rearrangement of aldoximes to amides via cobalt(II) acetate and 2-nitro-1-naphthol has also been demonstrated. A complete reversal of transformation was accomplished by modifying the cobalt salt and careful choice of both the nitrophenol ligand and reaction conditions.

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1. Introduction

Nitro compounds are important organic molecules in both academia and industrial settings although they are often highly explosive [1–3]. The nitration of organic molecules is a very straightforward and efficient method to introduce ‘the nitrogen atom’ into a molecular scaffold [1]. Nitro groups have been widely used in transition metal-catalyzed organic reactions due to its significant electron-withdrawing property. Meanwhile, transition metal–nitro complexes have been less widely studied despite the nitro group’s potential to coordinate directly to a metal center through one of the three heteroatoms. Coordination of the lanthanide metal by the nitro group is routinely used as a method of stabilization of explosive aromatic nitro compounds such as picric acid (trinitrophenol) series [3,4]. Since cobalt(II) salts have been widely studied in various organometallic complexes with tetradentate ligands such as Salen type molecules [5–7], we wondered whether an *ortho*-nitrophenol ligand could form metal–ligand complexes in a similar fashion. To the best of our knowledge, only two series of nitrophenol-coordinating cobalt complexes have been reported which studied

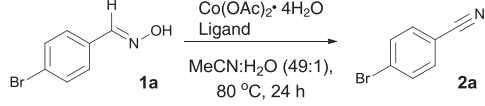
complex formation utilizing phosphine ligands and not for catalysis or other applications [8,9].

With the cobalt/nitrophenolate system, we attempted the conversion of aldoximes. Aldoximes are easily synthesized from aldehyde through stoichiometric reaction with hydroxylamine, and are key intermediates of various organic transformations. The aldoximes could be converted to primary amides in strong acidic conditions (i.e., Beckmann rearrangement), hydrolyzed to the corresponding aldehydes, changed to the amines through Hoffman reaction in the presence of alkali hypochlorites, or dehydrated to the corresponding nitrile compounds [2]. Recently, various late transition metal-catalyzed conversions of aldoximes have been reported, especially to formation of nitriles and amides [10–18]. The reaction pathway was dependent on both the transition metal and reaction conditions. For example, ruthenium catalyzed the dehydration of aldoximes to nitriles in acetonitrile with molecular sieve [10], whereas rhodium catalyzed the rearrangement of aldoximes to amides in toluene [13]. For the latter, high temperature (150 °C) or the addition of *p*-toluenesulfonic acid was essential to perform the reaction with good yields [15]. For cobalt, several complexes have been studied for the hydration of nitriles [19–21], but the dehydration of aldoximes [11,12] and direct conversion of aldoximes into amides are limited. Described herein is our study on the synthesis and characterization of cobalt/nitrophenolate complex, and their catalytic application to selective conversion of aldoximes into nitriles, through dehydration, and amides, through a rearrangement using cobalt(II) catalysts.

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Table 1
Screen of the dehydration reaction conditions.^a



| Entry | Catalyst system (mol%) | Yield ^b (%) |
|-------|---|------------------------|
| 1 | – | <1 |
| 2 | 3a (20) | <1 |
| 3 | Co(OAc) ₂ · 4H ₂ O (10) | 31 |
| 4 | Co(OAc) ₂ · 4H ₂ O (10) + 3a (20) | 90 |
| 5 | Co(OAc) ₂ · 4H ₂ O (10) + 3b (20) | 45 ^c |
| 6 | Co(OAc) ₂ · 4H ₂ O (10) + 3c (20) | 75 |
| 7 | Co(OAc) ₂ · 4H ₂ O (10) + 3d (20) | 45 ^c |
| 8 | Co(OAc) ₂ · 4H ₂ O (10) + 3e (20) | 45 ^c |
| 9 | Co(OAc) ₂ · 4H ₂ O (10) + CH ₃ COOH (20) | 39 |

^a Reaction condition: A mixture of 4-bromobenzaldoxime (0.25 mmol), cobalt catalyst (10 mol%) and ligand (if necessary) in acetonitrile (0.49 mL) and water (0.01 mL, 2 v/v% of water in acetonitrile) was stirred for 24 h at 80 °C.

^b Yield of isolated product, and is reported as an average from at least two independent measurements.

^c NMR yield, and is reported as an average from at least two independent measurements.

2. Experimental

Concentration of solution was carried out by using a rotary evaporator with a water aspirator, and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 Torr. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All chemicals were purchased from Sigma-Aldrich, TCI, and Alfa Aesar chemical companies.

2.1. Preparation of cobalt/nitrophenolate complex (**4**)

Cobalt acetate (1 mmol, 177 mg), 2,4-dinitrophenol (2 mmol, 368 mg) and anhydrous methanol (10 mL) were placed in a 50 mL round-bottom flask with a reflux condenser. The mixture was stirred at reflux for 1 day. After cooling, the precipitate was filtered, thoroughly washed with methanol (10 mL, 3 times). The solid was dried under vacuum to give a brown powder (259 mg, 56%). The single crystal of complex **4** was obtained from recrystallization in water.

2.2. Typical procedures for the synthesis of nitriles from aldoximes

Aldoxime (0.25 mmol), cobalt acetate(II) tetrahydrate (6.2 mg, 0.025 mmol), 2,4-dinitrophenol (9.2 mg, 0.05 mmol) and acetonitrile/

H₂O (0.49 + 0.01 mL, 2 v/v% of water in acetonitrile) were added to an oven-dried vial. The mixture was vigorously stirred at 80 °C for 24 h and then diluted with ethyl acetate. Solvent was removed in vacuo, and the desired product was purified and isolated by silica gel column chromatography (ethyl acetate/*n*-hexane).

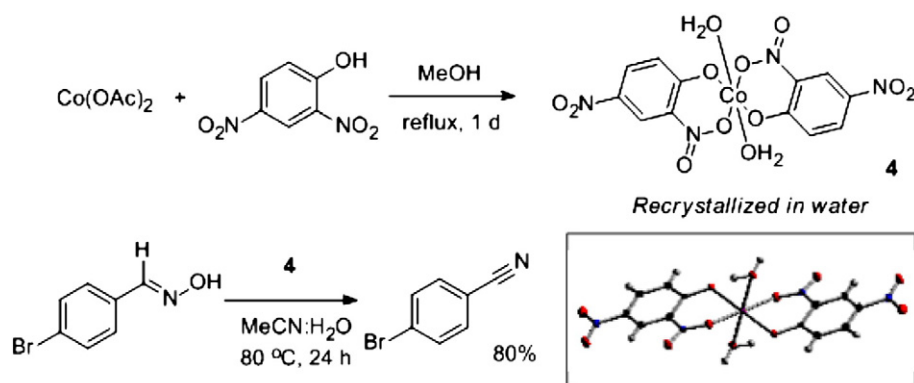
2.3. Typical procedures for the synthesis of amides from aldoximes

Aldoxime (0.25 mmol), cobalt acetate(II) tetrahydrate (6.2 mg, 0.025 mmol), 2-nitro-1-naphthol (9.5 mg, 0.05 mmol) and acetonitrile/H₂O (0.01 + 0.24 mL, 4 v/v% of acetonitrile in water) were added to an oven-dried vial. The mixture was vigorously stirred at 80 °C for 24 h and then diluted with ethyl acetate. Solvent was removed in vacuo, and the desired product was purified and isolated by silica gel column chromatography (ethyl acetate/*n*-hexane).

3. Result and discussion

Conversion of 4-bromobenzaldoxime (**1a**) to 4-bromobenzonitrile (**2a**) was explored as an initial test reaction (Table 1). Whereas no conversion of the benzaldoxime was observed in the absence of cobalt (entries 1 and 2), cobalt(II) acetate did display some catalytic activity on the test reaction (entry 3). One of the other side products from this reaction was identified as 4-bromobenzamide (6% yield). Acetonitrile was the solvent of choice with the addition of a small amount of water (2 v/v%) to improve solubility of the cobalt salt. This water and acetonitrile mixture produced higher product yields than either pure acetonitrile or water produced on their own. Interestingly, anions other than acetate were less effective. It was observed that 2,4-dinitrophenol (**3a**) was the highest yielding reactant (entry 4) among the various *ortho*-nitrophenol ligands screened (entries 4–8). This could be attributed to the inherent acidity of *ortho*-nitrophenol ligands by the electron withdrawing nature of the substituents. Among the ligands screened, 2,4-dinitrophenol ($pK_a = 4.11$) was the most acidic thus corroborating this hypothesis. A more acidic ligand, 2-nitrobenzoic acid ($pK_a = 2.16$) showed similar efficiency in the dehydration with an 85% yield. However, acidity of the ligand is not the only contributing factor in this improved reactivity. Acetic acid showed lower conversion than 2,4-dinitrophenol (**3a**) although they have similar pK_a s (entry 9).

To identify the active catalytic species, cobalt/nitrophenolate complex (Co(C₆H₃N₂O₅)₂(OH₂)₂, **4**) was synthesized. A brown powder was obtained from the reaction of cobalt(II) acetate with 2,4-dinitrophenol (**3a**), and was verified via X-ray crystallographic analysis (Scheme 1 and see Supporting information for detail, CCDC deposit 1009805). Since metal–nitro coordination complexes are rare, a detailed structure analysis was performed. The cobalt metal center has six coordinating oxygen atoms leading to an octahedral coordination geometry; two oxygen atoms from phenolate, two from



Scheme 1. Synthesis of cobalt/nitrophenolate complex (**4**) and its catalytic activity.

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