Tetrahedron Letters 54 (2013) 1558–1561

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Allylation of aldehydes with potassium allyltrifluoroborate catalyzed by lanthanide-based metal-organic framework

Juliano C. R. Freitas, Cristiane K. de Oliveira, Edilanio C. Cunha, Ivani Malvestiti *, Severino Alves Jr., Ricardo L. Longo, Paulo H. Menezes *

Departamento de Química Fundamental, Universidade Federal de Pernambuco, Recife, PE 50740-540, Brazil

ARTICLE INFO

Article history:
Received 27 December 2012
Accepted 8 January 2013
Available online 16 January 2013

Keywords:
Potassium organotrifluoroborates
Allylation
MOF catalysis

ABSTRACT

The use of the framework $[Eu_2(fum)_3(H_2O)_4]{\cdot}(3H_2O)$, Eu-MOF, as catalyst for allylation of aldehydes by potassium allyltrifluoroborate is described. The method features the use of small catalyst loads and wet solvents, and the products were obtained in high yields, short reaction times, at room temperature with no further purification. The catalyst was recovered and reused up to six times in further allylation reactions without significant loss in the yields.

Metal-organic frameworks (MOFs) are crystalline materials built with functionalized organic molecules that are linked by inorganic units to form porous solids with a regular and sometimes predictable structure.[1]

Because of their properties such as well-ordered microporosity, distinct organic linkers, variety of inorganic moieties, high surface area, and high absorption capacity, several applications in, for instance, catalysis,[2] gas storage,[3] separations,[4] and magnetism[5] have been studied. In particular, the field of catalysis using MOFs has experienced an impressive growth with a variety of applications in organic reactions such as Knoevenagel[6] and aldol condensations,[7] oxidation reactions,[8] epoxide formation[9] and ring-opening,[10] alkylation of amines,[11] cyclopropanation reactions,[12] hydrogenation,[13] Suzuki cross-coupling,[14] transesterification,[15] Friedel–Crafts reactions,[16] cyanosilylation,[17] and cyclization reactions.[18]

The development of methods focusing on environmentally benign reaction media has also been particularly prominent.[19] Thus, despite the advances in the use of supercritical fluids,[20] ionic liquids,[21] and fluorous media[22] the use of water as a (co)-solvent seems to be the best option due to its simplicity and very low cost.

In addition, catalytic methods that facilitate catalyst separation and recycling are very important and relevant to the synthesis of fine chemicals because they reduce the amount of waste products and energy consumption.[23]

The reaction of allylic organometallic reagents with aldehydes is synthetically analogous to the aldol addition of metal enolates, because the resulting homoallyl alcohol can be easily converted into aldol. Thus, the allylic organometallic reaction has attracted attention and allylation has become one of the most useful methods for controlling the stereochemistry in acyclic systems.[24]

Notwithstanding the several available methods for the allylation of carbonyl compounds in aqueous media based on, for example, In,[25] Sn,[26] Zn,[27] and Mg[28] derived reagents, organoboron compounds have proven to be very useful due to high yields and excellent stereocontrol. In this context, methods for the allylation of carbonyl compounds using allylic trifluoroborates promoted by Lewis acids[29] or palladium catalysts[30] have been described.

The high specific surface area and porosity make the metal-organic frameworks (MOFs) potential candidates for applications as both high-surface-area supports and intrinsic catalysts.[31] Syntheses and applications in catalysis of MOFs containing transition-metal ions are well known, but few examples using lanthanide ions were described, particularly due to the predictability of the coordination geometry of transition metal ions compared to lanthanide ions.[32]

In this Letter, we report the use of a porous 3D open-framework europium(III)-fumarate, $[Eu_2(fum)_3(H_2O)_4]{\cdot}(3H_2O)$, Eu-MOF, as a catalyst to promote the addition of potassium allyltrifluoroborate to aldehydes.[33]

In the course of developing milder reaction conditions, we first examined the effect of the solvent to promote the reaction. Thus, 4-NO_2-benzaldehyde, **1a** (1 mmol) and potassium allyltrifluoroborate, **2** (1.1 mmol) were treated at room temperature with catalyst

---

* Corresponding author. Tel.: +55 81 2126 7473; fax: +55 81 2126 8442.
E-mail address: paulo.menezes@pq.cnpq.br (P.H. Menezes).

0040-4039/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2013.01.035

(10 mol %) using different CH_2Cl_2/H_2O ratios, and the progress of the reaction was monitored by TLC. The results are presented in Table 1, and all reported yields in this and other tables are isolated yields.

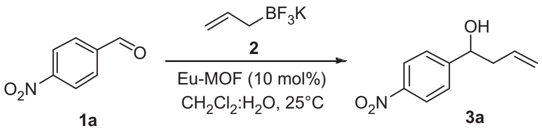
When only CH_2Cl_2 was used as the reaction solvent, a longer reaction time was required to promote the allylation reaction, probably due to the low solubility of potassium allyltrifluoroborate (Table 1, entry 1). For a 1:1 mixture of CH_2Cl_2/H_2O, a similar yield was observed; however, the reaction time was significantly decreased (Table 1, entry 2). By decreasing the amount of water it was observed that the reaction time also decreased with the yield remaining at ca. 90% (Table 1, entries 3–6). When only water was used as the reaction solvent **3a** was obtained in a lower yield, but at only 10 min (Table 1, entry 7).

Next we investigated the effect of the catalyst concentration on the reaction yield. The catalytic load of Eu-MOF was varied from 1 to 25 mol % (Table 2). It was observed that the reaction yield did not increase steadily with the amount of the catalyst. No significant changes in yields and reaction times were observed by using 25 or 10 mol % of catalyst (Table 2, entries 1 and 2). However, with further decreasing of the amount of catalyst the yield was slightly decreased and longer reaction times were required (Table 2, entries 3 and 4). In the absence of the catalyst, the product was obtained only in 7% yield after 15 min (Table 2, entry 5).

With the optimized reaction conditions, namely, 1:0.1 CH_2Cl_2/H_2O and 10 mol % of Eu-MOF, we extended the scope of the MOF-catalyzed allylation reaction to different aldehydes (Table 3). The method is robust to a wide range of functional groups with aliphatic, aromatic, α,β-unsaturated, and heterocyclic aldehydes being efficiently allylated in very high yields.

The electronic nature of the substituents in the aromatic aldehydes has little influence on the reaction. For example, the allylation of 4-NO_2- (Table 3, entry 1), 4-OCH_3- (Table 3, entry 6), 4-F- (Table 3, entry 15), 4-Cl- (Table 3, entry 16), and 4-Br-benzaldehyde (Table 3, entry 17) gave the corresponding products in high yields. Other aromatic aldehydes afforded good to high yields. Given the disparate electronic effects (*o*-, *m*-, and *p*-substituents, aromatic and aliphatic groups) associated with the aldehydes, the small differences in the isolated yields are more likely to be due to the solubilities of reactants and products. However, the differences in the reaction times might be related to the reactivity of the aldehyde because electron-donating substituents usually require longer reaction times. Also, the reaction appears to be regioselective because only 1,2-addition was observed for cinnamaldehyde (Table 3, entry 11). For aliphatic aldehydes, the Eu-MOF-catalyzed allylation also exhibited high efficiency (Table 3, entries 12 and 13).

Table 1
Effect of CH_2Cl_2/H_2O ratio on the allylation of 4-NO_2-benzaldehyde **1a** by potassium allyltrifluoroborate **2** catalyzed by Eu-MOF (10 mol %)



Entry	CH_2Cl_2/H_2O ratio (mL)	Time (min)	**3a** (%)
1	1:0	150	83
2	1:1	45	88
3	1:0.5	30	91
4	1:0.25	20	90
5	1:0.1	15	93
6	1:0.01	20	92
7	0:1	10	85

Table 2
Effect of the concentration of Eu-MOF on the allylation of 4-NO_2-benzaldehyde **1a** by potassium allyltrifluoroborate **2** in 1:0.1 CH_2Cl_2/H_2O at room temperature

Entry	MOF (mol %)	Time (min)	**3a** (%)
1	25	12	94
2	10	15	93
3	5	25	90
4	1	30	87
5	–	15	7

After each run, the catalyst was separated from the reaction mixture by centrifugation, washed with dichloromethane and reused. It was found that the Eu-MOF could be recovered and reused in further allylation reactions with no significant loss in the yields. However, the conversion of the aldehyde into the corresponding homoallylic alcohol required longer reaction times after each run (Table 4). Notice that no activation of the catalyst was performed in each run.

Eu^{3+} luminescence spectroscopy was employed to investigate the catalytic mechanism.[34] Photoluminescence emission of the pure Eu-MOF shows the typical transitions[34] $^5D_0 \rightarrow {}^7F_J$ ($J = 0–4$) of Eu^{3+} observed in the 550–720 nm range as shown in Figure 1, with $^5D_0 \rightarrow {}^7F_0$ being a very weak transition. Clearly, the emission spectra of the Eu-MOF as prepared and after the first catalytic run are very different. For instance, the lines were broadened and the relative intensities of the $^7F_1$ and $^7F_4$ transitions increased significantly in the spectrum of the solid (powder) after the first catalytic run. For being magnetically allowed the $^5D_0 \rightarrow {}^7F_1$ transition can be used as an internal standard of the Eu^{3+} coordination.[34] Thus, the differences in relative intensity ratios (see Table S1 in the Supplementary data) suggest that the environment around the Eu^{3+} changes when the catalyst is placed in the reaction medium. A mixture of Eu-MOF and potassium allyltrifluoroborate has a very similar luminescence spectrum as the reaction medium with the catalyst, whereas a mixture of MOF and 4-NO_2-benzaldehyde presents a spectrum practically identical to the pure catalyst. It might thus be inferred that the allyltrifluoroborate ion or its (partially) hydrolyzed species coordinates to the lanthanide center, possibly by displacing water ligands, and significantly alters the chemical environment.

The hydrolysis of organotrifluoroborates[35] is quite relevant to their reactivity and Eu-MOF can in fact assist this hydrolysis, because allylboronic acid may have more affinity to lanthanide ions by ligation through the hydroxyl groups.[36] On the other hand, this coordination could increase the reactivity of the allylborate species, thus exerting the catalytic effect. Considering the small sizes of the allyltrifluoroborate ion (molar volume of 133.7 $Å^3\ mol^{-1}$)[37] or its (partially) hydrolyzed species (e.g., allyltrihydroxyborate molar volume of 166.2 $Å^3\ mol^{-1}$),[37] they can fit within the cavities of the Eu-MOF[33] and coordinate to Eu^{3+} ion in the bulk of the solid and not only on surface.

These results suggest that Eu-MOF acts as a catalyst by activating the allyltrifluoroborate and/or its hydrolyzed products through coordination, and the aldehyde is expected to interact with the activated allylic species on the surface of the lanthanide-based MOF. This behavior can account for the reaction times and yields being practically independent of the size of the aldehyde (e.g., isobutyraldehyde (entry 12 in Table 3) and 2-naphthaldehyde (entry 9 in Table 3) have molar volumes of 107.3 and 221.5 $Å^3\ mol^{-1}$, respectively).[37] Alternatively, the Eu-MOF might catalyze the (partial) hydrolysis of allyltrifluoroborate yielding allylboronic acid derivatives, such as RB(F)OH and $RB(OH)_2$ ($R = CH_2{=}CHCH_2{-}$), which in solution are more reactive toward allylation and other reactions.[35] This also could explain the catalytic activity of the Eu-MOF as well as the observed allylation properties. A detailed