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Dariush Saberi, Akbar Heydari

PII: S0040-4039(13)00892-7
DOI: http://dx.doi.org/10.1016/j.tetlet.2013.05.113
Reference: TETL 43013

To appear in: *Tetrahedron Letters*

Received Date: 23 March 2013
Revised Date: 8 May 2013
Accepted Date: 24 May 2013

Please cite this article as: Saberi, D., Heydari, A., CuO nanoparticles supported on α-Fe_2O_3-modified CNTs: a magnetically separable catalyst for oxidative C-O coupling of formamides with 1,3-dicarbonyl compounds, *Tetrahedron Letters* (2013), doi: http://dx.doi.org/10.1016/j.tetlet.2013.05.113

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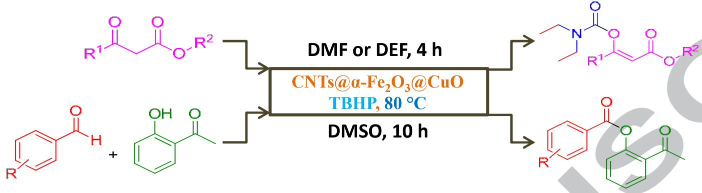


Tetrahedron Letters
journal homepage: www.elsevier.com

CuO nanoparticles supported on α-Fe_2O_3-modified CNTs: a magnetically separable catalyst for oxidative C-O coupling of formamides with 1,3-dicarbonyl compounds

Dariush Saberi, Akbar Heydari,*

Chemistry Department, Tarbiat Modares University, P.O. Box 14155-4838 Tehran, Iran, Fax: (+98)-21- 82883455; phone: (+98)-21-82883444; email: heydar_a@modares.ac.ir

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
CuO nanoparticles
Carbon nanotube
Enol carbamates
Magnetically separable catalyst
Oxidative coupling

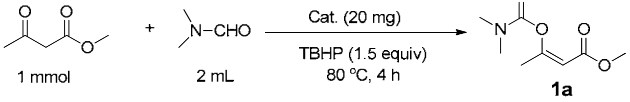
ABSTRACT

Oxidative coupling of formamides with 1,3-dicarbonyl compounds to prepare enol carbamates was effected in the presence of CuO nanoparticles supported on α-Fe_2O_3-modified carbon nanotubes (CNTs@α-Fe_2O_3@CuO) as an environmentally friendly heterogeneous catalyst. The simple preparation, and the ability to be recycled and magnetically separated are salient features of this catalytic system.

Carbamates show versatile applications as pesticides, insecticides, antibiotics, fungicidse and herbicides. In addition to their pharmacological properties,[1] some are used as protecting groups for amines in peptide synthesis.[2] Generally speaking, traditional methods for the synthesis of these compounds include the reaction of amines with phosgene or its derivatives, such as chloroformate,[3] dialkyl carbonates[4] or the reaction of alcohols with isocyanates.[5] Some drawbacks of these procedures are the extreme toxicity of the reagents used and the generation of by-products. Numerous efforts have been made to overcome these problems.[6] Transition metal catalyzed cross-coupling reactions have rendered traditional methods obsolete, since they provide an economic, short and facile method to form carbon-heteroatom bonds. Two methods have been reported for the synthesis of aryl carbamates and enol carbamates which exploit copper as the catalyst. In the first, arylboronic acids are reacted with potassium cyanate,[7] and in the second, oxidative C-O coupling by direct C-H bond activation of formamides has been accomplished.[8] The main problem of these reactions is that both suffer from loss of the catalyst at the end of the reaction. As a solution, the use of supports for catalysts has emerged which has led to heterogeneous catalytic systems. This approach is especially useful when a toxic and expensive transition metal is exploited as the catalyst. In this way, the catalyst can be recovered and reused, which is favorable from economic and environmental points of view.

Among the supports used, magnetic nanocomposites have warranted more attention because they can be easily recovered from the reaction mixture simply by using an external magnet.[9] We have reported the preparation of CuO nanoparticles supported on CNTs@α-Fe_2O_3, and its application as a highly efficient and magnetically separable catalyst for the synthesis of aryl ether derivatives based on Ullmann-type coupling.[10] In continuation of our interest in using magnetic nanoparticles as a catalyst support,[11] herein we report a green and environmentally benign catalytic system based on a magnetic support for the preparation of enol carbamates by oxidative C-O coupling of formamides with 1,3-dicarbonyl compounds. The utility of magnetic nanoparticles offers easy dispersion into the solution homogeneously, which facilitates catalyst recovery. The good catalytic activity of this system in C-O coupling reactions has led to its widespread use in coupling reactions. Simple separation by using an external magnet and the recyclability up to five times are two virtues of this system.

As shown in Scheme 1, the synthesis of compound **1a** was chosen as our model reaction to optimise the C-O coupling conditions.[12]



Scheme 1. Synthesis of enol carbamate **1a** catalyzed by CNTs@α-Fe_2O_3@CuO.

Only 15% of the product was obtained with 15 mg of the catalyst and TBHP (*tert*-butyl hydroperoxide) as the oxidant at room temperature (Table 1, entry 1). It was found that raising the reaction temperature to 80 ºC resulted in a drastic improvement in the yield (Table 1, entries 2 and 3).

Table 1. Results of screening the conditions.[a]

Entry	Oxidant	Catalyst (mg)	Temp. (°C)	Yield (%)[b]
1	TBHP	15	r.t.	15
2	TBHP	15	60	40
3	TBHP	15	80	55
4	TBHP	15	100	57
5	TBHP	20	80	71
6	TBHP	30	80	71
7	*m*CPBA	20	80	n.r.
8	H_2O_2	20	80	n.r.
9	UHP[c]	20	80	n.r.
10	NaOCl	20	80	n.r.
11	-	20	80	n.r.
12	TBHP	-	80	n.r.
13	TBHP	20	100	72

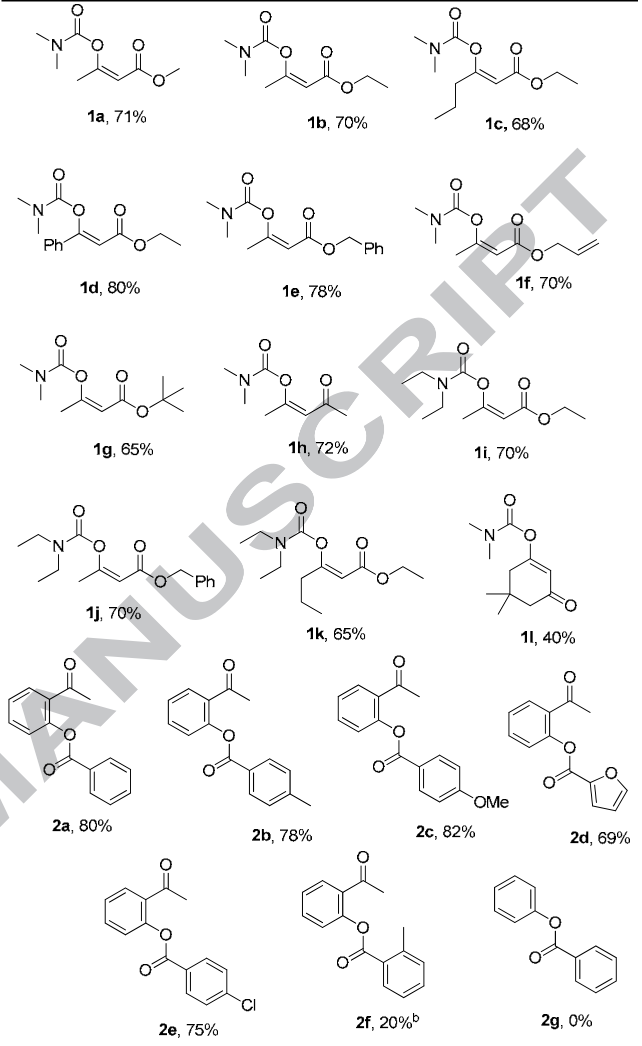
[a]All reactions were run with methyl acetoacetate (1 mmol), DMF (2 mL), TBHP (1.5 equiv), under Ar at 80 °C for 4 h. [b]Isolated yield. [c]Urea hydrogen peroxide

Increasing the temperature to 100 ºC did not enhance the yield noticeably (Table 1, entry 4). The reaction was then carried out in the absence of the catalyst and the oxidant, separately, which did not result in the formation of the product (Table 1, entries 11 and 12). This was indicative of the necessity of their presence in the reaction. The best result was obtained when 20 mg of the catalyst was used for 1 mmol of substrate (Table 1, entry 5). Among the oxidants used, TBHP was superior to H_2O_2, UHP, *m*CPBA, and NaOCl (Table 1, entries 7-10). Therefore, the optimum conditions for this reaction were as follows: 20 mg of catalyst at 80 ºC with the respective formamide as the solvent and TBHP as the oxidant (Scheme 1). Under these conditions, various 1,3-dicarbonyl compounds were used as substrates for the formation of the corresponding enol carbamates. In general, the desired enol carbamates were obtained in good yields with high stereoselectivity towards the *Z*-isomer. The nature of the 1,3-dicarbonyl compounds and dialkyl formamides did not have any profound influence on the reactivity (Table 2).

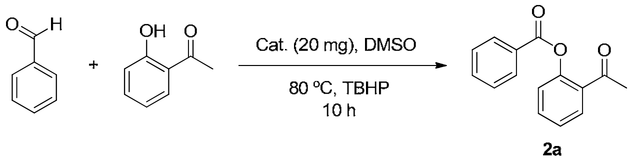
Following the successful C-O coupling of formamides with 1,3-dicarbonyl compounds, we were encouraged to extend this process to the C-O coupling of aldehydes with 2-hydroxyacetophenone to form phenol esters. The reaction between benzaldehyde and 2-hydroxyacetophenone was used as the model reaction. The conditions were almost the same as those described above (Scheme 2). The only difference was that, when DMF was used as the solvent, the coupling reaction between DMF and the 1,3-dicarbonyl compound competed with the main reaction. To prevent this happening, other solvents such as H_2O, EtOH, CH_3CN and DMSO were examined with DMSO giving the best result. Hence in this case the optimum conditions to prepare phenol esters were as follows: DMSO (2 mL), TBHP (1.5 equiv.), 20 mg of the catalyst at 80 ºC under an argon atmosphere (Table 2).[12]

The presence of an aldehyde substituent in the *para* position had little effect on the efficiency of the reaction, but substitution at the *ortho* position lowered the yield substantially (Table 2, product **2f**). It seems that steric factors were responsible for the decrease in efficiency. Furan-2-carbaldehyde was also coupled with 2-hydroxyacetophenone under these reaction conditions (Table 2, product **2d**). When phenol was employed instead of 2-hydroxyacetophenone, no product was formed. This indicates that coordination of the metal by the dicarbonyl compounds is one of the key factors of ester formation (Table 2, product **2g**). All these products were characterized by recording melting point (in some cases), IR, ^{1}H-NMR and ^{13}C-NMR spectra. The spectral data of two new compounds have been provided in the references and notes section.[13]

Table 2. Preparation of various enol carbamates in the presence of CNTs@α-Fe_2O_3@CuO.[a]



[a]Reactions conditions for the synthesis of compounds (**1a-l**): 1,3-dicarbonyl compound (1 mmol), formamide (2 mL), TBHP (1.5 equiv), Cat. (20 mg) under Ar at 80 °C for 4 h; reaction conditions for the synthesis of compounds (**2a-f**): phenol (1 mmol), aldehyde (1 mmol), DMSO (2 mL), TBHP (1.5 equiv), Cat. (20 mg) under Ar at 80 °C for 10 h. [b]GC yield



Scheme 2: Oxidative coupling of 2-hydroxyacetophenone with benzaldehyde

In the next step, the reusability of the catalyst was studied in the synthesis of compound **1a**. After completion of the first reaction between DMF and methyl acetoacetate, the catalyst was recovered using an external magnet, washed with H_2O and ethanol and oven-dried at 80 °C overnight. A new second reaction was then performed with fresh solvent and reactants under identical conditions. Using this approach, our catalyst could be reused at least five times without any further treatment, while no appreciable loss in the catalytic activity was observed (Figure 1). A hot filtration test was conducted to demonstrate the heterogeneous nature of the catalyst. For this purpose, the catalyst and the solvent were allowed to stir under the reaction conditions. After four hours the catalyst was removed from the reaction vessel using an external magnet and then the vessel was charged with acetoacetate and TBHP. The reaction progress was followed by TLC, which after four hours, showed no formation of product. This indicates that the CuO nanoparticles are stable on CNTs and do not leach.

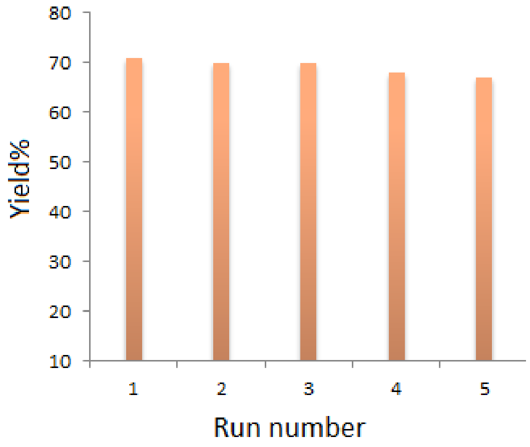


Figure 1: Recycling of the catalyst in the C-O coupling reaction of compound **1a** carried out for 4 h.

In summary, we have introduced an efficient strategy for the C-O cross-coupling of 1,3-dicarbonyl compounds with formamides to form enol carbamates, as well as oxidative coupling of 2-hydroxyacetophenone with aromatic aldehydes, using nano-CuO supported on magnetic CNTs as a heterogenous and magnetically separable catalyst. Its advantages include a straightforward preparation, facile separation from the reaction medium and recyclability up to five times.

Acknowledgments

We are thankful to Tarbiat Modares University for partial support of this work

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12. *General procedure:* TBHP (70 wt% in H_2O) was added dropwise to a mixture of the 1,3-dicarbonyl compound (1 mmol), catalyst (20 mg, 3.7 mol%) and *N*,*N*-dialkylformamide (2 mL). The reaction temperature was increased to 80 °C and the mixture was stirred for 4 h. After cooling to RT, the mixture was extracted with EtOAc (3x10 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded the crude product, which was purified by column chromatography to afford the desired product. For the oxidative esterification reactions, a slightly modified procedure was employed, which utilized DMSO as the solvent and the reaction time was increased to 10 h, giving rise to the formation of products (**2a-f**)
13. *(Z)-allyl 3-((dimethylcarbamoyl)oxy)hex-2-enoate (Table 2,* ***1f)*** Isolated yield = 70%; yellow oil; IR cm^{-1}: 750, 1035, 1145, 1211, 1271, 1320, 1382, 1669, 1727; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.06 (s, 3H, CH_3), 2.97 (s, 3H, CH_3N), 3.02 (s, 3H, CH_3N), 4.57 (dd, 2H, ^3J = 5.5 Hz, ^4J = 1.3 Hz, CH_2O), 5.18-5.34 (m, 2H, $\mathit{CH_2}$=CH), 5.58 (s, 1H, $\mathit{CH}CO_2$), 5.82-5.97 (m, 1H, CH_2=*CH*). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 22.20, 36.60, 64.62, 107.62, 118.03, 132.31, 153.01, 161.33, 163.66; MS (EI, 70 ev): *m/z* (%) = 213 (M^+, 8), 156 (64), 72 (100). Anal. Calcd for $C_{10}H_{15}NO_4$ (213.23): C, 56.33; H, 7.09; N, 6.57. Found: C, 56.25; H, 7.16; N, 6.47.
   2-Acetylphenyl 4-methoxybenzoate (Table 2, 2c) Isolated yield = 82%; white solid; mp: 94-96 °C; IR cm^{-1}: 610, 762, 963, 1069, 1364, 1481, 1683, 1724, 2965; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H, CH_3C=O), 3.84 (s, 3H, OCH_3), 6.94 (d, 2H, J = 9.2 Hz, CH of Ar), 7.16 (dd, 1H, ^3J = 8.0, ^4J = 0.8 Hz, CH of Ar), 7.29 (td, 1H, ^3J = 7.2 Hz, ^4J = 1.2 Hz, CH of Ar), 7.51(td, 1H, ^3J = 8.0 Hz, ^4J = 2.0 Hz, CH of Ar), 7.79(dd, 1H, ^3J = 7.6 Hz, ^4J = 1.6 Hz, CH of Ar), 8.10 (d, 2H, ^3J = 8.8 Hz, CH of Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.99, 55.58, 114.03, 121.49, 123.99, 126.07, 130.18, 131.52, 132.50, 133.35, 164.14, 190.75; MS (EI, 70 ev): *m/z* (%) = 270 (M^+, 5), 135 (100), 107 (25). Anal. Calcd for $C_{16}H_{14}O_4$ (270.28): C, 71.10; H, 5.22. Found: C, 71.02; H, 5.15.