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Copper Octoate: A Commercially Available and Cost-Effective Homogeneous Catalyst for the Facile Synthesis of 2,2′-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-ones)

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Abstract: A practical and convenient approach for the synthesis of 2,2′-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-ones) was presented using copper octoate as a homogeneous catalyst. Copper octoate as an eco-friendly, low cost, and commercially available catalyst, reduced reaction times effectively to (16-50 min) while the reaction profiles were absolutely clean and no side products including dehydrated xanthene heterocycle were detected. Pure target compounds were obtained in very good to excellent yields (83-91%) via straightforward work-up procedure. The catalyst was recycled in the form of solution, up to four times, with no noticeable drop in activity.

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Introduction

Application of transition metals as catalysts in organic reactions has achieved widespread acceptance within the synthetic organic community. The gradual realization that complexes of transition metals have a place in synthetic procedures has caused a quiet revolution. Today, there are very rare complex total syntheses that do not involve at least a few transition metal-mediated reactions as key steps. In fact, highly reactive and normally unavailable reaction intermediates can be generated by applying transition metal complexes, and be used as reagents in organic synthesis. Performing some of the metal-catalyzed organic reactions in relatively large scales shows that the aforementioned methods are more than just academic interest [1, 2].

Copper(II) 2-ethylhexanoate ($Cu(EH)_2$), or copper octoate (Figure 1), is a well-known industrial reagent. It has been used as a preservative in wood industry for several years [3] and is also applied for the preparation of superconductors [4-6]. Because of its long-lasting effect in protection against termites and other insects, it is usually applied in bottom paints of ships. In addition, copper octoate is utilized as rot-proofing agent in textiles and may be applied on textile fabrics by dipping or spraying. Moreover, as a fungicide and bactericide, it has found various applications in household and agricultural products to control a considerable range of plant diseases. Copper octoate has also been used as a catalyst in many organic transformations such as polymerizations [7], preparation of allylic alcohols, and alpha, beta-unsaturated carbonyl compounds from the rearrangement of epoxides [8], aldol reaction [9], oxidative coupling of indoles or pyrroles with enolates [10, 11] and oxidative coupling of esters or ketones with amides [12]. There is also a report of utilizing copper octoate as an ignition temperature-depressing agent which is applied as an additive to the fuel supply to promote oxidation of collected soot extracted from the exhaust gas of the engine [13]. An industrial example of using copper octoate as catalyst is its common application as a paint drier. Hydrocarbon chains help absorption of oxygen from the air and copper, on the other hand, acts as a catalyst to speed up the formation of the oxidative coating [14].

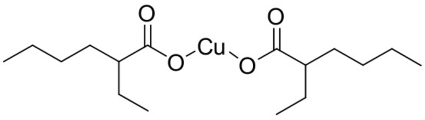


Figure 1. Copper octoate.

Copper octoate and many other metal complexes of 2-ethylhexanoic acid are often described as salts, while, indeed, they are not ionic but charge-neutral coordination complexes. The structure of copper octoate, both in crystalline [15] and solution [16] state, has been investigated. Low polarity and ionic character of copper octoate in addition to its long hydrocarbon chains are the major reasons for the high solubility of copper octoate in organic solvents like xylene and oils, which play a major role in finding extensive and novel applications both in industry and academia [17]. For instance, oxidative intramolecular cyclization of alkenyl amides was carried out successfully in the presence of copper octoate while its acetate salt did not perform well. It was mentioned as a reason that copper octoate has both the comparable activity with copper acetate and a high solubility in the reaction medium which causes homogeneity in the reaction medium [18]. Indeed, combining less toxicity and non-corrosive nature of solid acids and the motility of liquid acids, is the uniqueness of this Lewis acid which makes it a promising catalyst in the field of organic synthesis. Copper octoate is commercially available with quite low costs and in the form of solvated in organic solvents in various grades and with different metal content and solvents which can be manufactured upon customer's demand.

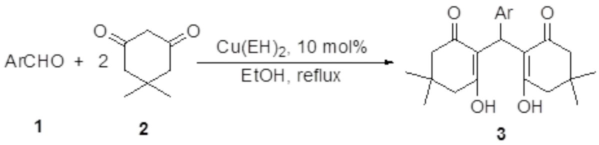
Arylmethylene bis(3-hydroxy-2-cyclohexene-1-one) derivatives belong to the family of tetraketones which are used as valuable intermediates for the synthesis of various heterocycles such as acridines, xanthenes, and thiaxanthenes which contain structures including dihydropyridine, pyran, and thiapyran [19]. These compounds have applications in laser technology [20] as well as clinical uses as antioxidant [21], tyrosinase [22], and lipoxygenase [21] inhibitors.

The first report about the synthesis and characterization of this class of compounds was by George Merling and in the course of preparing 1,3-cyclohexanedione from resorcinol [23]. Nevertheless, the principle synthetic avenue to arylmethylene bis(3-hydroxy-2-cyclohexene-1-ones) comprises the condensation of an aldehyde with a two-fold excess of 1,3-cyclohexanedione derivatives. This reaction was utilized for identification and characterization of aldehydes and was carried out in aqueous ethanolic solution catalyzed by piperidine [24].

So far, various reaction conditions have been presented for this reaction including, $CaCl_2$ in chloroform [25], palladium nanoparticles in water [26], urea in water under ultrasonic irradiation [27], $FeCl_3.6H_2O$ and TMSCl in [bmim][BF_4] [28], I_2 in water [29] and ethylenediamine diacetate in THF [30]. Regarding practical, environmental and economic aspects, most of these methods may not be appropriate for industrial applications.

There are also some catalyst-free approaches using water [31], dichloromethane [32] or DMF [33] as solvents and grinding technique [34]. However, long reaction times associated with these catalyst-free reactions, sometimes up to 24 or 48 hours, remarks the necessity of using a catalyst for this reaction.

In this paper, copper octoate has been applied as a homogeneous catalyst for the convenient synthesis of 2,2′-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-ones) (MbHDMC). Copper octoate exhibited pronounced catalytic activity and was easily separated by simple filtration (Scheme 1).



Scheme 1. Synthesis of MbHDMC (3) using copper octoate as catalyst.

Experimental

All the chemicals were purchased from Merck and Sigma-Aldrich companies. Melting points were measured by using the capillary tube method with an Electrothermal 9200 apparatus. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AQS AVANCE-400 MHz spectrometer, using TMS as an internal standard ($CDCl_3$ solution). FT-IR spectra were recorded on the FT-IR Bruker Tensor 27. Elemental analyses (% C, H, N) were carried out by Perkin-Elmer 2400 CHN elemental analyzer.

Synthesis of Copper Octoate

Although this complex is widely available and could be purchased in quite low costs, an example of its preparation has been provided to illustrate the simplicity involved in it which could be counted as another advantage for extending its applications.

To a solution of 2-ethylhexanoic acid (98%, 0.12 mol, 18.00 g) in 100 mL of xylene in a round-bottomed flask, sodium hydroxide (0.12 mol, 5.00 g) solution in 50 mL of water was added. Next, the mixture was stirred and a solution of copper sulfate pentahydrate (0.06 mol, 15.00 g) in 50 mL of water was added drop wise. The mixture was stirred for 1 hour and then the two phases were separated. The organic phase was washed with water and dried by azeotropic distillation in the form of a binary azeotrope of water and xylene, from which the water is removed by distillation using a Dean-Stark apparatus.

General procedure for the synthesis of MbHDMCs using copper octoate as catalyst

To a solution of aldehyde (1 mmol) and dimedone (2 mmol, 0.28 g) in ethanol (5 mL), a solution of copper octoate in xylene (6%, 0.1 mmol, 0.58 g) was added. The solution was refluxed for the amount of time indicated in Table 2. After completion of the reaction as monitored by TLC, using petroleum ether:ethyl acetate (4:1, v:v) as eluent, the reaction mixture was cooled to room temperature and then the precipitated product was simply filtered and washed with ethanol. The catalyst was easily removed to the filtrate in the solvated form in ethanol. For further purification, the products were recrystallized from ethanol. All of the products were known and their physical data were compared with those of authentic samples in the literature and found to be identical.

Physical and spectral data

2,2′-phenylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3a)

Mp: 191 °C; FT-IR (KBr): 3423, 2842, 1593, 1498, 1314, 871 cm^{-1}; ^{1}H-NMR (δ, 400 MHz, CDCl$_3$): 1.15 (s, 6H, 2CH$_3$), 1.27 (s, 6H, 2CH$_3$), 2.31–2.56 (m, 8H, 4CH$_2$), 5.54 (s, 1H, CH), 7.08–7.28 (m, 5H, ArH), 9.76 (s, 1H, OH), 11.89 (s, 1H, OH); ^{13}C-NMR (δ, 100 MHz, CDCl$_3$): 26.5, 29.7, 30.1, 32.8, 46.7, 47.4, 116.6, 124.3, 125.5, 128.7, 138.3, 190.4, 190.8; Anal. Calcd. for $C_{23}H_{28}O_4$: C%, 74.97; H%, 7.66. Found: C%, 74.62; H%, 7.71.

2,2′-(4-methoxyphenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3b)

Mp: 147 °C; FT-IR (KBr): 3596, 1794, 1620, 1403, 1175 cm^{-1}; ^{1}H-NMR (δ, 400 MHz, CDCl$_3$): 1.15 (s, 6H, 2CH$_3$), 1.65 (s, 6H, 2CH$_3$), 2.34–2.42 (m, 8H, 4CH$_2$), 3.81 (s, 3H, OCH$_3$), 5.81 (s, 1H, CH), 6.61 (d, *J*= 8.1 Hz, 2H, ArH), 6.88 (d, *J*= 8.1 Hz, 2H, ArH), 12.06 (brs, 2H, OH); ^{13}C-NMR (δ, 100 MHz, CDCl$_3$): 26.8, 29.2, 31.0, 31.9, 45.2, 46.8, 55.9, 113.3, 115.7, 127.5, 129.2, 157.1, 189.1, 190.4; Anal. Calcd. for $C_{24}H_{30}O_5$: C%, 72.34; H%, 7.59. Found: C%, 72.24; H%, 7.75.

2,2′-(3-nitrophenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3c)

Mp: 194-196 °C; FT-IR (KBr): 3394, 2972, 1599, 1379 cm^{-1}; 1H-NMR (δ, 400 MHz, CDCl$_3$): 1.10 (s, 6H, 2CH$_3$), 1.05 (s, 6H, 2CH$_3$), 2.36-2.58 (m, 8H, 4CH$_2$), 5.55 (s, 1H, CH), 7.45-7.50 (m, 2H, ArH), 8.00-8.08 (m, 2H, ArH), 11.85 (brs, 2H, 2OH); ^{13}C-NMR (δ, 100 MHz, CDCl$_3$): 27.22, 29.70, 31.44, 32.85, 46.43, 46.99, 113.12, 121.07, 123.22, 129.16, 133.88, 141.65, 148.46, 189.68, 194.15; Anal. Calcd. for $C_{23}H_{27}NO_6$: C%, 66.81; H%, 6.58; N%, 3.39. Found: C%, 66.73; H%, 6.80; N%, 3.12.

2,2′-(4-nitrophenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3d)

Mp: 190 °C; FT-IR (KBr): 2962, 1533, 1513, 1375, 1345 cm^{-1}; ^{1}H-NMR (δ, 400 MHz, CDCl$_3$): 1.11(s, 6H, 2CH$_3$), 1.18 (s, 6H, 2CH$_3$), 2.47 (m, 8H, 4CH$_2$), 5.58 (s, 1H, CH), 7.22 (d, *J*= 8.9 Hz, 2H, ArH), 8.17 (d, *J*= 8.9 Hz, 2H, ArH), 9.77 (s, 1H, OH), 11.79 (s, 1H, OH); ^{13}C-NMR (δ, 100 MHz, CDCl$_3$): 27.0, 29.6, 32.5, 33.3, 45.4, 47.0, 114.8, 123.1, 127.8, 146.0, 146.4, 189.8, 190.8; Anal. Calcd. for $C_{23}H_{27}NO_6$: C%, 66.81; H%, 6.58; N%, 3.39. Found: C%, 66.65; H%, 6.83; N%, 3.24.

2,2′-(4-methylphenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3e)

Mp: 142 °C; FT-IR (KBr): 3421, 2963, 2640, 1685, 1477, 1383, 1160, 892 cm^{-1}; ^{1}H-NMR (δ, 400 MHz, CDCl$_3$): 1.15 (s, 6H, 2CH$_3$), 1.24 (s, 6H, 2CH$_3$), 2.32–2.54 (m, 8H, 4CH$_2$), 5.46 (s, 1H, CH), 2.76 (s, 3H, CH$_3$), 6.91–7.24 (m, 3H, ArH), 11.58 (s, 1H, OH), 11.92 (s, 1H, OH); Anal. Calcd. for $C_{24}H_{30}O_4$: C%, 75.36; H%, 7.91. Found: C%, 75.37; H%, 7.69.

2,2′-(4-N,N-dimethylaminophenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3f)

Mp: 195-197 °C; FT-IR (KBr): 3132, 1605, 1521, 1377, 1315, 1268, 811 cm^{-1}; ^{1}H-NMR (δ, 400 MHz, CDCl$_3$): 0.99 (s, 6H, 2CH$_3$), 1.28 (s, 6H, 2CH$_3$), 2.30–2.50 (m, 8H, 4CH$_2$), 3.09 (s, 6H, N(CH$_3$)$_2$), 5.46 (s, 1H, CH), 6.69 (d, *J*= 8.4 Hz, 2H, ArH), 6.98 (d, *J*= 8.4 Hz, 2H, ArH), 9.53 (s, 1H, OH),11.95 (s, 1H, OH); Anal. Calcd. for $C_{25}H_{33}NO_4$: C%, 72.96; H%, 8.08; N%, 3.40. Found: C%, 72.90; H%, 8.23; N%, 3.24.

2,2′-(4-hydroxyphenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3g)

Mp: 190 °C; FT-IR (KBr): 3425, 3083, 1595, 1498, 1374, 1322 cm^{-1}; ^{1}H-NMR (δ, 400 MHz, CDCl$_3$): 1.08 (s, 6H, 2CH$_3$), 1.22 (s, 6H, 2CH$_3$), 2.45 (m, 8H, 4CH$_2$), 5.41 (s, 1H, CH), 6.82 (d, *J*= 8.8 Hz, 2H, ArH), 7.01 (d, J= 8.8 Hz, 2H, ArH), 9.48 (s, 1H, OH), 11.91 (brs, 2H, 2OH); ^{13}C-NMR (δ, 100 MHz, $CDCl_3$): 27.4, 29.4, 31.2, 32.0, 46.7, 47.2, 115.4, 115.9, 128.0, 129.5, 153.6, 189.5, 190.7; Anal. Calcd. for $C_{23}H_{28}O_5$: C%, 71.85; H%, 7.34. Found: C%, 71.67; H%, 7.78.

2,2’-(4-bromophenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3h)

Mp: 173-176 ^{o}C; FT-IR (KBr): 3463, 2994, 2865, 1743, 1731, 1601 cm^{-1}; ^{1}H-NMR (δ, 400 MHz, $CDCl_3$): 1.14 (s, 6H, $2CH_3$), 1.28 (s, 6H, $2CH_3$), 2.19–2.45 (m, 8H, $4CH_2$), 5.49 (s, 1H, CH), 7.00 (d, *J*= 6.6 Hz, 2H, ArH), 7.39 (d, *J*= 6.6 Hz, 2H, ArH), 11.94 (brs, 2H, 2OH); ^{13}C-NMR (δ, 100 MHz, $CDCl_3$): 27.41, 29.66, 31.23, 32.48, 46.44, 47.14, 115.56, 119.63, 128.65, 131.89, 137.22, 189.45, 190.75; Anal. Calcd. for $C_{23}H_{27}BrO_4$: C%, 61.75; H%, 6.08. Found: C%, 61.42; H%, 6.12.

Results and Discussion

Initially, benzaldehyde was selected as a typical aromatic aldehyde in order to optimize parameters such as the amount of catalyst, solvent, and temperature. The reaction between benzaldehyde (1 mmol) and dimedone (2 mmol) was carried out in ethanol and under reflux. After one hour, the product was obtained in 69% yield. However, in the presence of 15 mol% of copper octoate as catalyst, the yield of the target compound (**3a**) increased to 90% and the reaction time decreased to 25 min which highlights the effect of the catalyst. To optimize the amount of catalyst, the model reaction was carried out in the presence of different quantities of catalyst. As shown in Table 1, the best result was with 10 mol% of the catalyst. In the next step, we switched to decide the best reaction medium by running the model reaction in other solvents like acetonitrile and chloroform, but no improvement was observed in reaction profiles. Various temperatures were also examined disclosing the fact that the reaction shows a great dependence on temperature and higher temperatures are preferable in terms of reaction times and yields.

With these initial results in hand, we next examined the generality of this method using different aromatic aldehydes with various substitution patterns. These results are collected in Table 2. Under the optimized conditions, irrespective of the substituent present on aromatic ring, the corresponding products were obtained with high yields and purity by simple filtration.

For many years, these target compounds were considered as tetraketones. However, according to spectral data and X-ray diffraction studies [33], a keto-enol form has now been assigned to this class of compounds as the major structure. For example, in ^{1}H-NMR spectra of **3a**, three singlet protons have been appeared in 11.89, 9.76, and 5.54 ppm which are attributed to hydroxyl protons and the benzylic proton connected to linker carbon, respectively. The singlet form of these peaks negates the presence of any adjacent proton to the aforementioned protons, which occurs in tetraketone frameworks. In addition, hydroxyl absorption in 3423 cm^{-1} and carbonyl absorption in 1593 cm^{-1} in the FT-IR spectra, are other evidences which give more clarification to recommended keto-enol structure.

Table 1. Optimization of the conditions for the model reaction of benzaldehyde with dimedone.

Entry	Amount of catalyst (mol%)	Solvent	Temperature (⁰C)	Time (min)	Yield (%)
1	0	EtOH	Reflux	60	69
2	5	EtOH	Reflux	40	90
3	10	EtOH	Reflux	24	91
4	15	EtOH	Reflux	25	90
5	20	EtOH	Reflux	25	88
6	10	CH_3CN	Reflux	32	85
7	10	$CHCl_3$	Reflux	30	84
8	10	EtOH	25	60	87
9	10	EtOH	40	45	88
10	10	EtOH	60	30	91

Table 2. Synthesis of various MbHDMCs catalyzed by copper octoate[a].

Entry	Ar	Product	Time (min)	Yield (%)	mp (⁰C)	
					Found	Reported
1	C_6H_5	**3a**	24	91	191	190-191 [35]
2	4-$OMeC_6H_4$	**3b**	35	88	147	146-148 [25]
3	3-$NO_2C_6H_4$	**3c**	16	89	194-196	190-191 [27]
4	4-$NO_2C_6H_4$	**3d**	20	90	190	189 [35]
5	4-MeC_6H_4	**3e**	50	91	142	139-141 [25]
6	4-$N(Me)_2C_6H_4$	**3f**	27	88	195-197	195-196 [34]
7	4-OHC_6H_4	**3g**	45	89	190	189 [35]
8	4-BrC_6H_4	**3h**	40	88	173-176	172-174 [28]

[a]Reaction Conditions: aldehyde (1 mmol), dimedone (2 mmol), 6% xylene solution of copper octoate (0.1 mmol, 0.58 g), EtOH (5 mL), reflux.

On the other hand, according to the symmetrical appearance of the structures of the products, it is initially expected that ^{1}H-NMR spectrum of these compounds would be clear and uncrowded ones exhibiting two hydroxyl protons in the same chemical shift; while in fact, the number of signals are more than what was anticipated and hydroxyl groups appeared at δ 11.89 and 9.76 ppm. These distinguished chemical shifts disclose the asymmetric character of the structure of the product which could be simply explained by the intramolecular hydrogen bonds, decreasing the asymmetry of the molecule effectively (Figure 2). Indeed, the formation of intramolecular hydrogen bonds restricts the rotation around the methylene bridge and locks the molecule in a rigid asymmetric form in which one of the hydroxyl groups is settled close to the benzylic proton and probably corresponds to the high-field signal while the other hydroxyl proton next to the Ar group is related to the low-field signal. In other words, the methylene bridge acts as a chiral center inducing a diastereotopic relationship between the hydroxyl groups. Kaupp et al. demonstrated the presence of intramolecular hydrogen bonds as two almost identical O-H…O hydrogen bridges by B3LYP/6-31G calculations. The formation of these hydrogen bridges was attributed to molecular tendency for minimizing its energy levels [35]. Similar interpretations were also made by several groups to illustrate the presence of intramolecular hydrogen bonds in bis(coumarin) derivatives [36-38] (Figure 2).

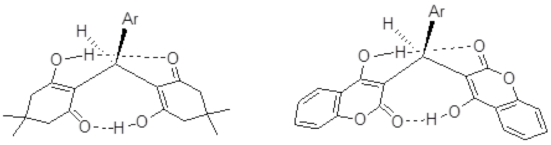


Figure 2. Intramolecular hydrogen bonding in MbHDMC and biscoumarin derivatives.

A possible mechanism for this reaction is demonstrated in Figure 3. Lewis acid-catalyzed Knoevenagel condensation of aldehyde (**1**) and dimedone (**2**) results in the formation of the intermediate (**4**), which on addition of the second molecule of dimedone, the target MbHDMC (**3**) is formed. The blockage of the reaction at this stage, the reluctance for dehydration of (**3**), and formation of the corresponding xanthene could be attributed to the mild essence of copper octoate and also the fact that the desired product (**3**) gradually precipitates from the reaction solution and practically interrupts the function of homogeneous copper octoate catalyst.

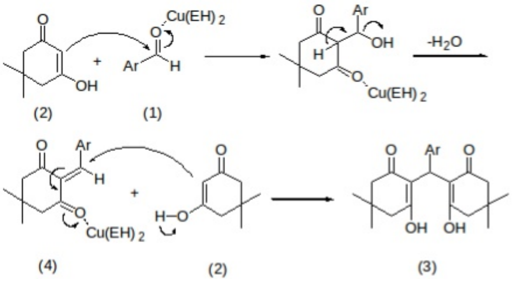


Figure 3. Plausible mechanism for the copper octoate-catalyzed synthesis of MbHDMCs.

After completion of each reaction, the reaction mixture was cooled to room temperature and the precipitated product was simply filtered and washed with ethanol. For evaluating the reusability of the catalyst, the filtrate was heated to remove the excess of ethanol and reduce the volume to approximately 5.6 mL (the amount of ethanol required as solvent for the next run plus the xylene solution of the copper octoate). To the concentrated solution remained, the starting materials of the model reaction were simply added and the resulted solution was heated to reflux. As it is exhibited in Table 3, the recycled catalyst solution promoted reactions in a similar manner without significant loss of activity.

In order to prove the merit of copper octoate functioning as a homogeneous catalyst in the synthesis of MbHDMCs,the results obtained for the model reaction in the present work has been compared with previously reported methods in Table 4.

As it is obviously illustrated, the yield obtained using copper octoate as catalyst is almost comparable to other catalysts and conditions but reaction time has been shortened remarkably to amount which is rarely achieved by other approaches presented.

Table 3. Evaluating the reusability of the catalyst.

Run	Yield (%)
1	91
2	88
3	89
4	85

Table 4. Comparison of the efficiency of copper octoate with other reagents and conditions for the synthesis of (**3a**)

Entry	Catalyst	Condition/Solvent	Time (h)	Yield (%)	Reference
1	Urea	US, 50 ^{0}C/H_2O	1	94	[27]
2	ZnO	reflux, CH_3CN	12	92	[39]
3	$HClO_4$-SiO_2	reflux, H_2O	0.5	91	[40]
4	EDDA[a]	reflux, THF	4	88	[30]
5	N/A	Ball-milling 100 ^{0}C, neat	1	100	[35]
6	N/A	grinding RT, neat	0.67	86	[34]
7	N/A	RT, CH_2Cl_2	24	69	[32]
8	Pd nanoparticles	reflux, H_2O	0.3	88	[26]
9	$CaCl_2$	RT, $CHCl_3$	13	69	[25]
10	KF/Al_2O_3	grinding RT, neat	0.33-0.66	86	[41]
11	$FeCl_3.6H_2O$+TMSCl	80 ^{0}C [bmim][BF_4]	6	89	[28]
12	N/A	80 ^{0}C/DMF	1	80	[33]
13	Cu(EH)$_2$	reflux, EtOH	0.4	91	[b]

[a] Ethylenediamine diacetate.

[b] This work.

Conclusion

In summary, copper octoate as an extensively used industrial reagent has been introduced as a mild Lewis acid catalyst for the synthesis of MbHDMCs. Fine tuning of reaction conditions such as the strength of the catalyst and even solvent plays a critical role in controlling progress of the reaction in the desired level since harsh reaction conditions may result in cyclodehydration and formation of the byproduct of xanthene. In this reaction, the dramatic effect of copper octoate being acidic enough to accelerate the reaction up to very short times in one hand and mild enough to terminate reaction after formation of Michael adducts on the other hand, is quite noticeable. This behavior could be useful in lots of other synthetic processes. In fact, non-corrosive and green character, low cost, and commercial availability are features making it a superior choice as catalyst in organic transformations specially those having an emphasize on the homogeneity of the catalyst.

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