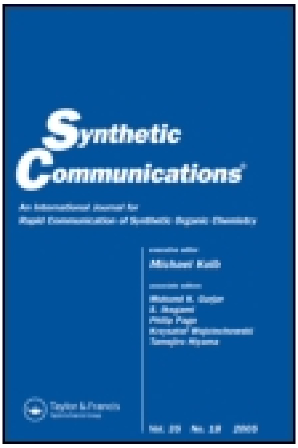

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$CuSO_4 \cdot 5H_2O$: A Novel, Green, Reusable, and Environmentally Friendly Catalyst for the One-Pot, Four-Component Synthesis of β-Acetamido Carbonyl Compounds

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$CuSO_4 \cdot 5H_2O$: A NOVEL, GREEN, REUSABLE, AND ENVIRONMENTALLY FRIENDLY CATALYST FOR THE ONE-POT, FOUR-COMPONENT SYNTHESIS OF β-ACETAMIDO CARBONYL COMPOUNDS

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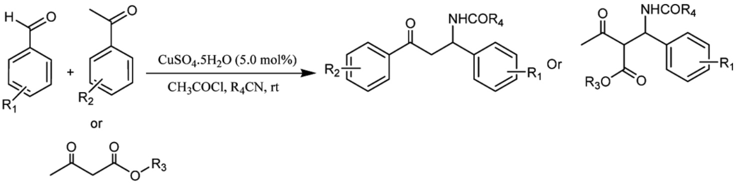
GRAPHICAL ABSTRACT



Abstract *Multicomponent reactions for the synthesis of β-acetamido carbonyl compounds have been gained considerable attention in organic synthesis. In this articles, aromatic aldehydes have been employed in a one-pot reaction with enolizable ketones, acetonitrile, benzonitrile, and acetyl chloride in the presence of copper(II) sulfate petahydrate at ambient temperature to afford the corresponding* β*-acetamido ketones in very good yields. New compounds are reported. The use of readily available copper(II) sulfate petahydrate as a reusable and recyclable catalyst makes this process quite simple, convenient, and environmentally friendly.*

Keywords β-Acetamido carbonyl compounds; catalyst; $CuSO_4 \cdot 5\,H_2O$; MCRs; reusable

INTRODUCTION

Recently, $CuSO_4 \cdot 5H_2O$ has been used as a Lewis acid catalyst for various organic transformations such as tetrahydropyranylation–depyranylation of alcohols and phenols,[1] protection of alcohols and phenols using hexamethyldisilazane,[2] the one-pot conversion of tetrahydropyrane (THP) ethers to acetates,[3] the chemoselective synthesis of 1,1-diacetates from aldehydes,[4] the synthesis of quinoxaline derivatives,[5] the synthesis of β-keto esters,[6] the one-pot synthesis of β-hydroxytriazoles from epoxides,[7] and the synthesis of 1,2,3-triazoles.[8] It is an inexpensive, available,

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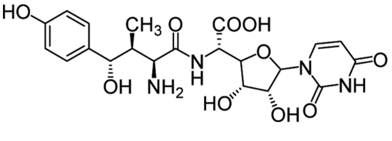
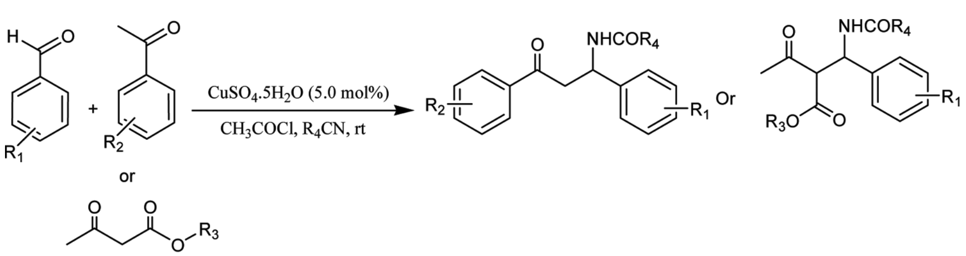


Scheme 1. Nicomycine.

and extremely safe reagent in chemical reactions. Nowadays, multicomponent reactions (MCRs) are a promising and vital field of chemistry because of the rapid and efficient synthesis of complicated molecules without the need to isolation intermediates. It requires minimum effort, which minimizes the environmental loading and is acceptable from a "green chemistry" point of view.

The MCRs for the synthesis of β-acetamido carbonyl compounds have gained considerable attention in organic synthesis. The products, containing of β-acetamido carbonyl skeletons, are found in a number of biologically or pharmalogically important compounds such as nikkomycine and neopolyoxines (Scheme 1).[9–11] Recently it has been reported that β-acetamido ketones can act as α-glocosidase inhibitors.[12]

The best-known route for the synthesis of these compounds is the Dakin–West reaction,[13] which involves the condensation of an α-amino acid with acetic anhydride in the presence of a base via an azalactone intermediate.[14] After that, a number of catalysts such as $CoCl_2$,[15] montmorillonite K-10 clay,[16] $Cu(OTf)_2$/$Sc(OTf)_3$,[17] silica-supported sulfuric acid,[18] BiOCl,[19] $H_3PW_{12}O_{40}$,[20] $ZrOCl_2 \cdot 8H_2O$,[21] I_2,[22] Amberlyst-15,[23] $CeCl_3 \cdot 7H_2O$,[24] $H_6P_2W_{18}O_{62}$,[25] $FeCl_3 \cdot 6H_2O$,[26] ZnO,[27] $K_5CoW_{12}O_{40} \cdot 3H_2O$,[28] sulfamic acid (SA),[29] heteropolyacid,[30] sulfated zirconia,[31] zirconium(IV) chloride,[32] ZnO nanoparticles,[33] $Fe(ClO_4)_3 \cdot 6H_2O$,[34] cerium(IV) sulfate,[35] polyaniline-supported acid catalyst,[36] $Zr(HSO_4)$, $Mg(HSO_4)$,[37] and Select Flur[38] have been reported as effective catalysts for the synthesis of β-acetamido carbonyl compounds. However, these procedures have drawbacks such as long reaction times,[15] high catalyst loadings,[27] or the necessity for freshly prepared catalyst.[18,20,25] Therefore, there is a need for a greener and catalytically efficient method, which might work under mild and economically cheaper conditions. In this communication and in continuing our works in catalytic and MCRs under ecofriendly and solvent-free conditions,[39–43] we disclose a mild and



R_1= H, 4-Nitro, 3-Nitro, 4- Methyl, 4-Bromo, 4-Chloro, 2-Methoxy, 4-Methoxy
R_2= H, 4-Nitro, 4-Methoxy
R_3= Me, Et, Bn
R_2= Me, Ph

Scheme 2. Synthesis of β-acetamido carbonyl compounds using $CuSO_4 \cdot 5H_2O$.

efficient multicomponent condensation reaction utilizing $CuSO_4 \cdot 5H_2O$ as a green, inexpensive, cost-effective, nontoxic, and commercially catalyst for the synthesis of β-amido carbonyl compounds in the presence of aromatic aldehyde derivatives; acetophenone derivatives; benzyl, ethyl, and methyl acetoacetate; acetyl chloride; acetonitrile; and benzonitrile at room temperature (Scheme 2).

RESULTS AND DISCUSSION

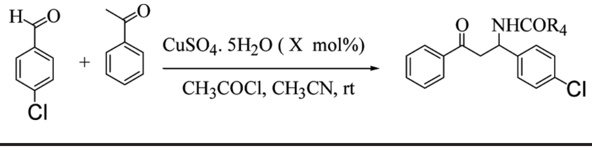
To demonstrate the catalytic nature of $CuSO_4 \cdot 5H_2O$, an experiment was conducted in which the reaction of benzaldehyde, acetophenone, acetyl chloride, and acetonitrile was studied in the absence of catalyst. The reaction was not completed even after 24 h. Obviously, the catalyst is an essential component of the reaction.

In three separate reactions, a mixture of 4-chlorobenzaldehyde (2.0 mmol), acetophenone (2.0 mmol), acetyl chloride (3.0 mmol), acetonitrile (3.0 mmol), and different amounts of $CuSO_4 \cdot 5H_2O$ (5.0, 2.5, 1.0 mol%) were stirred at room temperature without solvent. The conversion was completed within 4.5 h, and the best result was obtained using 5.0 mol% of $CuSO_4 \cdot 5H_2O$ in 92% yield (Table 1). Thus, entry 4 of Table 1 was selected, and the reactions were continued under similar conditions.

To prove the generality of the optimized reaction conditions, a variety of aldehydes with electron-donating and electron-withdrawing groups on the aromatic ring and enolizable ketones such as acetophenone, 4-nitroacetophnone, and benzyl, ethyl and methyl acetoacetate were also subjected to Dakin–West reaction in the presence of $CuSO_4 \cdot 5H_2O$ as catalyst. The results showed that the naturality of groups did not affect the reaction time and yields (Table 2).

In all cases, complete conversion was observed after an appropriate time and the products were isolated in very good yields. β-Acetamido ketones were also prepared from β-keto esters by the reaction of aromatic aldehydes, acetonitrile, and acetyl chloride in the presence of $CuSO_4 \cdot 5H_2O$ (Table 2, entries 20–25). In almost all cases, *anti* products were only monitored by ^1H NMR spectra (Table 2, entries 24 and 25), while most articles reported a mixture of *anti* and *syn* compounds as products.[26] Interestingly, it was also found that the products of entries 24 and 25 had not previously been prepared and so they were new compounds. Physical and spectral data of the entries 24 and 25 have been put in the experimental section.

Table 1. Optimization of $CuSO_4 \cdot 5H_2O$ for the synthesis of β-acetamido-β-(4-chlorophenyl) propiophenone



Entry	X (mol%)	Time (h)	Yield (%)
1	0	24	15
2	1	12	75
3	2.5	9	80
4	5	4.5	92

Table 2. Synthesis of β-acetamido carbonyl compounds was catalyzed using $CuSO_4 \cdot 5H_2O$ in the presence of aldehydes, enolizable ketones and ester, acetyl chloride, benzonitrile, and acetonitrile

							Mp (°C)	
Entry	R1	R2	R3	R4	Time (h)	Yield (%)	Observed	Reported
1	H	H		Me	5.0	92.5	102–104	102–104[27]
2	H	H		Ph	6.0	93.0	151–154	153–154[26]
3	H	4-NO_2		Me	6.0	95.0	101–102	101–103[37]
4	H	4-OMe		Me	4.0	91.0	128–129	127–129[29]
5	4-NO_2	H		Me	8.5	94.0	148	148–149[16]
6	4-NO_2	H		Ph	9.0	90.0	143–145	142–144[26]
7	4-NO_2	4-NO_2		Me	8.5	95.0	176–180	176–179[37]
8	4-NO_2	4-OMe		Me	6.0	88.0	110–112	84–86[35]
9	3-NO_2	H		Me	7.0	89.0	136–139	139–140[21]
10	3-NO_2	4-NO_2		Me	7.2	92.0	180–181	—
11	3-NO_2	4-OMe		Me	5.0	94.0	130	130–131[35]
12	4-Me	H		Me	5.5	87.0	Oil	112–114[44]
13	4-Me	4-NO_2		Me	5.8	81.0	83–84	83–85[16]
14	4-Br	H		Me	4.5	90.0	147–149	147–149[44]
15	4-Cl	H		Me	4.5	92.0	144–146	145–147[35]
16	4-Cl	H		Ph	6.0	94.0	177–180	180–182[26]
17	2-OMe	H		Me	6.0	90.0	138–140	—
18	2-OMe	4-NO_2		Me	5.0	92.0	183–184	—
19	4-OMe	H		Me	4.5	94.0	110–112	110–112[21]
20	H		Me	Me	3	82	128–130	128–130[26]
21	4-Cl		Me	Me	3	84	130–131	131–133[26]
22	4-Br		Me	Me	3	83	110–112	160–161[15]
23	4-Br		Et	Me	3	81	119–120	120–122[44]
24[a]	H		Ben	Me	3	88	134–135	—
25[a]	4-Cl		Ben	Me	3	80	149–151	—

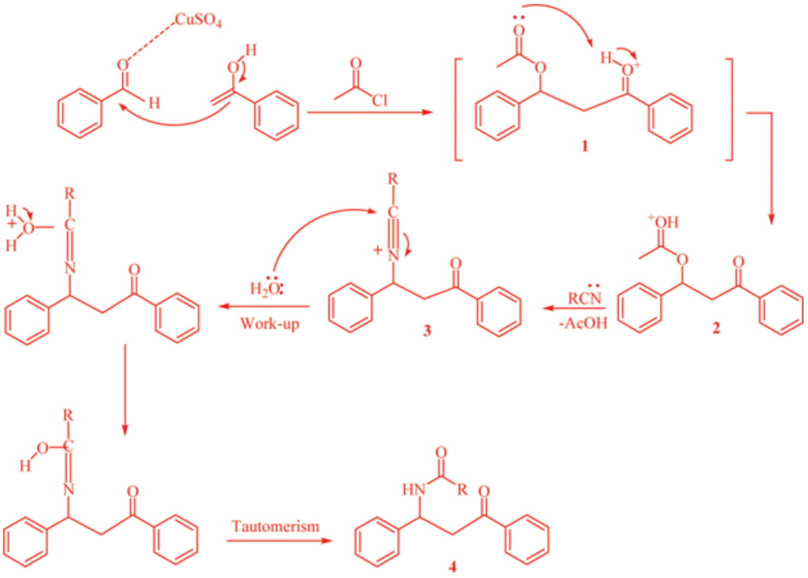
[a] New compounds.

$CuSO_4 \cdot 5H_2O$ was chosen as the catalyst because of its moisture stability, recoverability, and reusability without any loss of the catalytic activity. Therefore, this method provides β-amido carbonyl compounds in simple, efficient, and novel green protocol directly. The mechanism[17,27] may involve the enolic form of the ketone, which attacks the activated aldehyde to provide a product **2** after exchange of H^+ from **1**. Next, the nitrile attacks **2** with elimination of acetate to give **3**. Hydrolysis of **3** accompanied by tautomerization gave the desired β-amido ketone **4** (Scheme 3).

To show the merits and advantages of using copper(II) sulfate as a catalyst in the synthesis of N-(3-oxo-1,3-diphenylpropyl) acetamide, our protocol was compared with previously reported methods (Table 3). From the results given in Table 3, the advantages of our method are evident regarding the yields of the reactions, which are very important in the chemical industry especially when it is combined by easy separation.

CONCLUSION

In conclusion, the present work describes a simple, efficient, and green protocol for the preparation of β-amido carbonyl compounds using $CuSO_4 \cdot 5H_2O$ as a



Scheme 3. Suggested mechanism for the reaction. (Figure is provided in color online.)

reusable catalyst. The salient features of this procedure include very easy workup, good yields of the products, avoidance of column chromatography, easy and safe handling, no toxicity, reusability of the catalyst, and synthesis of some new β-acetamido carbonyl compounds.

EXPERIMENTAL

Melting points were measured by using the capillary tube method with an Electrothermal 9200 apparatus. Infrared (IR) spectra were recorded on a Perkin-Elmer Fourier transform (FT)–IR spectrometer with scanning between 4000 and 400 cm^{-1}. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker DRX 400-MHZ NMR instrument. Chemicals shifts are reported in parts per million (S) relative to tetramethylsilane (S 0.0) as internal standard. Elemental analyses were performed by elemental analyzer Vario EL. Analytical thin-layer chromatography (TLC) of all reactions was performed on Merck precoated plates (silica gel 60 F-254 on aluminium). All starting materials purchased from Merck Company and used without more purification.

Synthesis of β-Acetamido Ketone and Esters: General Procedure

A mixture of ketone or benzyl, ethyl, and ethyl acetoacetate (2.0 mmol), aldehyde (2.0 mmol), and acetyl chloride (3.0 mmol) in acetonitrile/benzonitrile (3.0 mmol) was treated with a catalytic amount of $CuSO_4 \cdot 5H_2O$ (5.0 mol%) at room temperature. The progress of reaction was monitored by TLC. Upon completion of the reaction, a mixture of crushed ice (50 ml) was added to the reaction mixture. The

Table 3. Various of catalysts were used in the one-pot, three-component synthesis of N-(3-oxo-1,3-diphenylpropyl) acetamide

Catalyst	Amount (mol%)	Time (h)	T (°C)	Yield (%)[Ref]
Montmorilonite K-10	2g	7	70	80[45]
Silica sulfuric acid	78	1.08	80	91[18]
Sc(OTf)$_3$	10	30	Rt	82[17]
Cu(OTf)$_2$	10	30	Rt	64[17]
Bi(oTf)$_3$	10	30	Rt	69[17]
I_2	10	4.5	Rt	85[22]
BiCl$_3$ or BiOCl	20	7	Rt	92[19]
LiClO$_4$	100	0.5	Rt	59[26]
InCl$_3$	100	0.5	Rt	19[26]
$H_3PW_{12}O_{40}$	5	0.83	Rt	95[20]
$ZrOCl_2 \cdot 8H_2O$	20	5	Rt	90[21]
$CeCl_3 \cdot 7H_2O$	10	7	Rt	96[24]
Amberlyst-15	0.2 g	6	Rt	89[23]
ZnO	50	6	80	90[28]
NH_2SO_3H	5	1.41	Rt	90[29]
$FeCl_3 \cdot 6H_2O$	10	8	Rt	88[33]
CuO	50	20	80	40[27]
Fe_2O_3	50	20	80	65[27]
CdO	50	18	80	35[27]
TiO_2	50	18	80	20[27]
ZnO	50	6	80	90[27]
Nafion-H	0.5 g	4	Rt	96[46]
Heteropolyacid	0.7	0.41	80	86[25]
ZnO bulk	10	4	Rt	55[33]
ZnO nanoparticles	10	1	Rt	83[33]
CeSO$_4$	20	3.5	85	83[35]
Mg(HSO$_4$)$_2$	20	0.83	Rt	89[37]
Zr(HSO$_4$)$_2$	20	0.5	Rt	90[37]
ZrCl$_4$	20	5	Rt	80[37]
MgCl$_2$	20	20	Rt	30[37]
PANI-H$_2$SO$_4$	4.8	1	50	90[36]
$CuSO_4 \cdot 5H_2O$	5	5	Rt	92 (this work)

precipated solid was filtered off. The residue was washed with 20 ml of water, and the crude product was recrystallized from ethyl acetate/n-hexane.

Recycling of the Catalyst

At the end of reaction, ice water was added to the reaction mixture. The precipated solid was filtered off. Then liquid mother was evaporated, and the catalyst was removed, washed with dichloromethane and ethyl acetate, dried at 65 °C for 3 h, and reused in another reaction (three runs). The recycled catalyst was subjected to three reactions without observation of appreciable loss in its activity.

Physical and Spectral Data for New Compounds

Benzyl 2-(acetamido(phenyl)methyl)-3-oxobutanoate (Table 2, Entry 24). Mp 134–135 °C; white solid IR (KBr): 3368.02 (s), 1736.18 (s), 1715.30 (s), 1650.52 (s), 1528.70 (s), 1458.03 (m), 1373.60 (s), 1293.46 (s), 1244.49 (m), 1140.59 (s), 1097.10 (s), 705.25 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 1.93$ (s, 3H, NHCOC$\underline{H}_3$), 2.13 (s, 3H, CHCOC$\underline{H}_3$), 4.12 (d, $J = 7.98$ Hz, 1H, $\underline{CH}$COCH_3), 5.11 (s, 2H, OC$\underline{H}_2$Ph), 5.78 (dd, $J = 11.95$ Hz, 1H, C$\underline{H}$NHCOCH_3), 6.94 (d, $J = 11.47$ Hz, Hz, 1H, N$\underline{H}$), 7.28 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 203.2, 170.8, 170.0, 143.5, 141.2, 128.6, 127.2, 68.5, 65.1, 57.9, 28.1, 33.6. Elem. anal. $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13; O, 18.86.

Benzyl 2-(acetamido(4-chlorophenyl)methyl)-3-oxobutanoate (Table 2, Entry 25). Mp 149–151 °C; white solid. IR (KBr): 3366.24 (m), 1739.29 (s), 1718.12 (m), 1651.24 (s), 1526.22 (s), 1456.25 (w), 1361.20 (m), 1294.42 (s), 1242.56 (m), 1142.41 (s), 1092.07 (m), 694.34 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 1.92$ (s, 3H, NHCOC$\underline{H}_3$), 2.14 (s, 3H, CHCOC$\underline{H}_3$), 4.08 (d, $J = 8.01$ Hz, 1H, $\underline{CH}$COCH_3), 5.11 (s, 2H, OC$\underline{H}_2$Ph), 5.70 (dd, $J = 11.97$, 1H, C$\underline{H}$NHCOCH_3), 6.89 (d, $J = 11.91$ Hz, 1H, N$\underline{H}$), 7.36–7.28 (m, 9H, Ar). ^{13}CNMR ($CDCl_3$, 400 MHz) δ 203.2, 170.8, 170.0, 141.2, 132.0, 128.4, 127.2, 68.5, 65.1, 57.9, 28.1, 23.6 ppm. Elem. anal. $C_{20}H_{20}ClNO_4$: C, 64.26; H, 5.39; Cl, 9.48; N, 3.75; O, 17.12.

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