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An Efficient, Ligand-Free, Heterogeneous Supported Copper Hydroxide Catalyst for the Synthesis of *N*,*N*-Bicyclic Pyrazolidinone Derivatives

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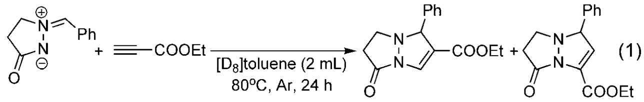
The synthesis of pyrazolidinone and pyrazolone heterocycles is of great importance because they have been used as dyes, color pigments, pharmaceuticals, and agricultural chemicals.[1] In particular, *N*,*N*-bicyclic pyrazolidinone derivatives show very important bioactivities and have been widely investigated as pesticides, herbicides, and analogues of β-lactam antibiotics such as penicillin and cephalosporin.[2] The 1,3-dipolar cycloaddition of azomethine imines to alkynes (an analogous reaction to the Huisgen 1,3-dipolar cycloaddition[3]), first reported by Dorn and Otto in 1968,[4] is one of the most useful procedures for the synthesis of *N*,*N*-bicyclic pyrazolidinone derivatives because many functional groups remain intact in the presence of azomethine imines and alkynes.[2] However, this uncatalyzed cycloaddition gives a mixture of regioisomers in the case of unsymmetrically substituted alkynes;[5] for example, when the thermally induced cycloaddition of 1-benzylidene-3-oxo-1-pyrazolidinium-2-ide (**1a**) to ethyl propiolate (**2a**) was carried out under the conditions described in Equation (1), a regioisomeric mixture of **3aa** and **3aa′** was obtained.



(1)

1a (0.5 mmol) **2a** (0.55 mmol) **3aa** (78% yield) **3aa′** (19% yield)

Generally, it is widely accepted that the 1,3-dipolar cycloaddition of organic azides to terminal alkynes proceeds regioselectively in the presence of copper catalysts and that a (in situ generated) copper(I) acetylide is the catalytically active species.[6] Similarly, Fu and co-workers reported for the first time that the 1,3-dipolar cycloaddition of azomethine imines to terminal alkynes also proceeds regioselectively in the presence of copper(I) salts and certain nitrogen-based ligands.[7] Although copper-catalyzed cycloaddition is a powerful method for the synthesis of *N*,*N*-bicyclic pyrazolidinone derivatives, only a few catalysts have been reported until now; for example, CuI/nitrogen-based ligands,[7] $[Cu(\mu\text{-}OH)(tmen)]_2Cl_2$ (tmen = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine),[8] and copper(I)-exchanged zeolites.[9] In addition, these systems have shortcomings such as 1) low turnover frequency (TOF) and turnover number (TON), 2) difficulty in catalyst/product(s) separation and catalyst reuse, and/or 3) indispensability of additives such as stabilizing ligands. Therefore, the development of efficient catalysts (in particular, heterogeneous catalysts are desirable[10]) for the cycloaddition is still a challenging subject.

Herein, we report that the 1,3-dipolar cycloaddition is efficiently promoted by the easily prepared inexpensive supported copper hydroxide catalyst, $Cu(OH)_x/Al_2O_3$.[11] Various kinds of azomethine imines and terminal alkynes could be utilized as dipoles and dipolarophiles, respectively, to form the corresponding *N*,*N*-bicyclic pyrazolidinone derivatives in moderate to high yields. In addition, the observed catalysis was truly heterogeneous, and $Cu(OH)_x/Al_2O_3$ could be reused with retention of its high catalytic performance.

Initially, the catalytic activities for the 1,3-dipolar cycloaddition of **1a** to **2a** were compared for various copper-based catalysts. The supported copper hydroxide $Cu(OH)_x/Al_2O_3$ (see the Experimental Section for the preparation and characterization) showed the highest catalytic activity and gave the corresponding *N*,*N*-bicyclic pyrazolidinone **3aa** in an almost quantitative yield (Table 1, entry 1). It was confirmed by the ^1H NMR analysis that the $Cu(OH)_x/Al_2O_3$-catalyzed cycloaddition exclusively gave **3aa** without the formation of the regioisomer **3aa′**. The cycloaddition hardly proceeded in the absence of the catalysts (Table 1, entry 10) or in the presence of Al_2O_3 (Table 1, entry 9). The catalyst precursor $CuCl_2{\cdot}2H_2O$ and commonly utilized copper salts such as CuCl and $CuSO_4{\cdot}5H_2O$ were not effective for the cycloaddition (Table 1, entries 3–5). The catalytic activity of $Cu(OH)_x/Al_2O_3$ was much higher than those of CuO, unsupported $Cu(OH)_2$, and a physical mixture of $Cu(OH)_2$ and Al_2O_3 (Table 1, entries 6–8). The catalytic activity of $Cu(OH)_x/Al_2O_3$ was higher than that of $CuCl_2$ supported on Al_2O_3 prepared without the base treatment ($CuCl_2/Al_2O_3$, see the Supporting Information for the preparation) (Table 1, entry 1 vs. entry 2). These results suggest that the generation of the "*highly dispersed copper hydroxide species*" on the surface of supports is very important to achieve high catalytic performance.

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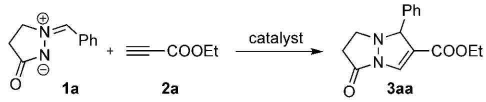
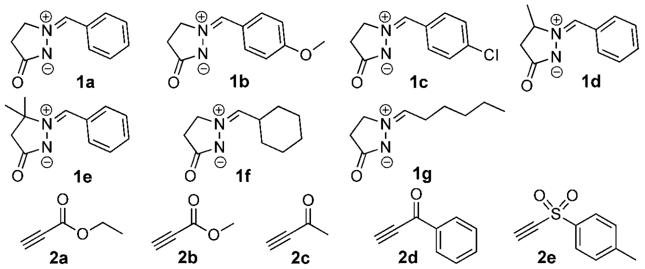
Table 1. 1,3-Dipolar cycloaddition reaction of **1a** to **2a** with various copper catalysts.[a]



Entry	Catalyst	Yield of **3aa**[b] [%]
1	$Cu(OH)_x/Al_2O_3$	95
2	$CuCl_2/Al_2O_3$	45
3	$CuCl_2 \cdot 2H_2O$	2
4	$CuCl$	3
5	$CuSO_4 \cdot 5H_2O$	1
6	CuO	3
7	$Cu(OH)_2$	<1
8[c]	$Cu(OH)_2 + Al_2O_3$	4
9[d]	Al_2O_3	4
10	none	3

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.55 mmol), catalyst (Cu: 1.5 mol% with respect to **1a**), [D_8]toluene (2 mL), 40 °C, Ar (1 atm), 2.5 h. [b] Yields (based on **1a**) were determined by ^{1}H NMR spectroscopy. [c] A mixture of $Cu(OH)_2$ (Cu: 1.5 mol%) and Al_2O_3 (30 mg). [d] Al_2O_3 (30 mg).

Table 2. $Cu(OH)_x/Al_2O_3$-catalyzed 1,3-dipolar cycloaddition of azomethine imines (dipoles) to terminal alkynes (dipolarophile).[a]



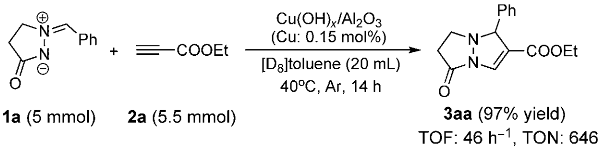
Entry	Dipole	Dipolarophile	Product	*t* [h]	Yield[b] [%]
1	**1a**	**2a**	**3aa**	2.5	95
2[c]	**1a**	**2a**	**3aa**	2.5	94
3[c]	**1a**	**2a**	**3aa**	2.5	93
4	**1a**	**2b**	**3ab**	2.5	96
5	**1a**	**2c**	**3ac**	4.5	97
6	**1a**	**2d**	**3ad**	24	55
7	**1a**	**2e**	**3ae**	3.5	88
8	**1b**	**2a**	**3ba**	4.5	93
9	**1c**	**2a**	**3ca**	2	92
10	**1d**	**2a**	**3da**[d]	4	98
11	**1e**	**2a**	**3ea**	12	80
12	**1f**	**2a**	**3fa**	2.5	88
13	**1g**	**2a**	**3ga**	12	85

[a] Reaction conditions: dipole (0.5 mmol), dipolarophile (0.55 mmol), $Cu(OH)_x/Al_2O_3$ (Cu: 1.5 mol% with respect to dipoles), [D_8]toluene (2 mL), 40 °C, Ar (1 atm). [b] Yields (based on dipoles) were determined by ^{1}H NMR spectroscopy. [c] Reuse experiments; entry 2 (the 1st reuse) and entry 3 (the 2nd reuse). [d] *syn*/*anti* = 86:14. The ratio was determined by ^{1}H NMR spectroscopy.

To examine whether the observed catalysis is derived from the solid $Cu(OH)_x/Al_2O_3$ catalyst or leached copper species, the cycloaddition of **1a** to **2a** was carried out under the conditions described in Table 1, and the $Cu(OH)_x/Al_2O_3$ catalyst was removed from the reaction mixture by filtration at approximately 50% conversion of substrates. After removal of the $Cu(OH)_x/Al_2O_3$ catalyst, **1a** (0.25 mmol) was newly added to the filtrate, and the resulting solution was again heated at 40 °C under an Ar atmosphere. In this case, no further production of **3aa** was observed. In addition, it was confirmed by inductively coupled plasma atomic emission spectroscopy that copper species were hardly detected in the filtrate (below 7 ppm after the cycloaddition). These results rule out any contribution to the observed catalysis from copper species that leached into the reaction solution, and the observed catalysis is heterogeneous.[12]

Next, the scope of the $Cu(OH)_x/Al_2O_3$-catalyzed cycloaddition was examined. The cycloaddition of azomethine imine **1a** (as a dipole) to various terminal alkynes bearing electron-withdrawing groups (as dipolarophiles) including propargylic esters (**2a** and **2b**), propargylic ketones (**2c** and **2d**), and tosylacetylene (**2e**) gave the corresponding *N*,*N*-bicyclic pyrazolidinone derivatives in moderate to high yields (Table 2, entries 1 and 4–7). Various kinds of azomethine imines could be utilized as dipoles for the present cycloaddition. As for the azomethine imines with *para*-substituted benzylidene groups at the dipole ends (**1a**–**1c**), the reaction rates of the dipoles with electron-withdrawing substituents were larger than those with electron-donating ones (Table 2, entries 1, 8, and 9). Monomethyl- (**1d**) and dimethyl-substituted (**1e**) dipoles at the 5-positions also gave the corresponding *N*,*N*-bicyclic pyrazolidinone derivatives in high yields (Table 2, entries 10 and 11), whereas these reactions required longer reaction times in comparison with that of unsubstituted **1a** because of the steric hindrance of methyl groups in **1d** and **1e**. The cycloaddition of monomethyl-substituted **1d** to **2a** showed a high *syn* diastereoselectivity for the methyl and phenyl groups in **3da** (*syn*/*anti* = 86:14) (Table 2, entry 10), suggesting that the addition of an alkyne (acetylide species) mainly takes place *anti* to the methyl group in **1d**. Also, dipoles with alkyl groups at the dipole ends (**1f** and **1g**) worked well as reaction partners of dipolarophiles (Table 2, entries 12 and 13). The $Cu(OH)_x/Al_2O_3$ catalyst retrieved after the cycloaddition could be reused without an appreciable loss of its high catalytic performance; for the cycloaddition of **1a** to **2a** with the retrieved catalyst under the conditions described in Table 2, 94% and 93% yields of **3aa** were obtained for the 1st and the 2nd reuse experiments, respectively (Table 2, entries 2 and 3).

Notably, the amount catalyst required could be reduced considerably; in a 5 mmol-scale cycloaddition of **1a** to **2a** using only 0.15 mol% of $Cu(OH)_x/Al_2O_3$ (at 40 °C), the TOF was 46 h^{-1}, and the TON reached up to 646 [Eq. (2)]. These values were much higher than those previously reported for the copper-based heterogeneous catalyst of copper(I)-exchanged zeolite (TOF: 4.5 h^{-1}, TON: 18 at 60 °C).[9]



(2)

The $Cu(OH)_x/Al_2O_3$ catalyst (Cu: 1.4 mol% with respect to **2a**) was treated with **2a** in [D$_8$]toluene (0.27 M, 2 mL) at 40 °C for 1 h under an Ar atmosphere, and the UV/Vis spectrum of the retrieved catalyst was measured. The intensity of the absorption band around 700 nm assignable to the d–d transition of copper(II) species[13] decreased considerably (Figure 1, inset). Furthermore, it was confirmed by the GC-MS analysis that the corresponding diyne (**4aa**)[14] was produced during the treatment. These results suggest that the following reduction of copper(II) to copper(I) species by an alkyne likely proceeds at the initial stage of the cycloaddition (step (i) in Scheme 1) [Eq. (3)].[15]

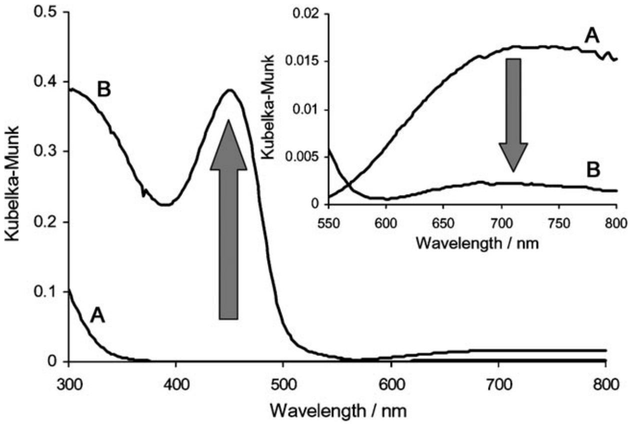
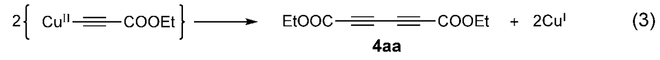
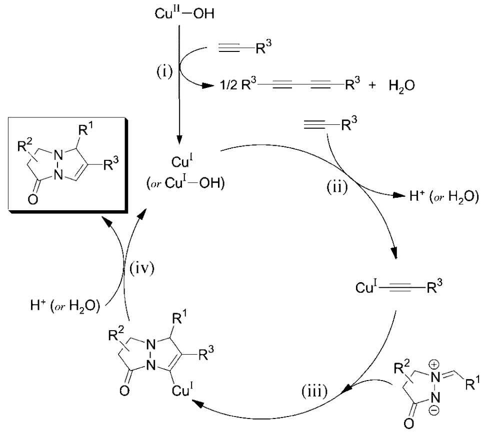


Figure 1. The UV/Vis spectra of the fresh $Cu(OH)_x/Al_2O_3$ catalyst (spectrum A) and the catalyst retrieved after the treatment with **2a** (spectrum B).



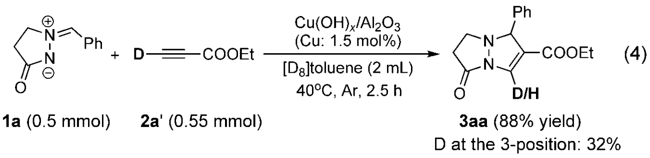
$$2\{Cu^{II}-\!\!\equiv\!\!-COOEt\} \longrightarrow \underset{\mathbf{4aa}}{EtOOC-\!\!\equiv\!\!-\!\!\equiv\!\!-COOEt} + 2Cu^{I} \qquad (3)$$

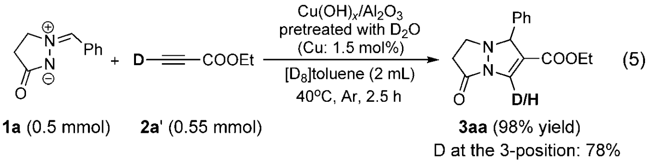
In addition to a decrease in the intensity of the d–d transition band, a new broad absorption band around 450 nm assignable to copper(I) acetylide species appeared (Figure 1),[16] suggesting that the reaction of the copper(I) species with an alkyne takes place to generate the catalytically active copper(I) acetylide species (step (ii) in Scheme 1).[17] Upon treatment of the catalyst (treated with **2a**) with **1a** (two equiv) in [D$_8$]toluene (2 mL) at 40 °C for 2.5 h, the absorption band due to the acetylide species disappeared with the formation of an almost equimolar amount of **3aa** (37.1 μmol) with respect to the copper species used (33.5 μmol). The reaction of the acetylide species with an azomethine imine likely proceeds to form the corresponding vinyl copper species (step (iii) in Scheme 1),[9] followed by the ligand exchange between the vinyl copper species and proton (or water) to form the corresponding *N,N*-bicyclic pyrazolidinone and the copper(I) species (step (iv) in Scheme 1), and the catalytic cycle is completed.



Scheme 1. A possible reaction mechanism for the present $Cu(OH)_x/Al_2O_3$-catalyzed cycloaddition.

The cycloaddition of **1a** to deuterated ethyl propiolate **2a′** (D content at the terminal position: 94%)[18] gave **3aa** in 88% yield, and the deuterium content at the 3-position of **3aa** was 32% [Eq. (4)]. When the 1,3-dipolar cycloaddition of **1a** to **2a′** was carried out in the presence of $Cu(OH)_x/Al_2O_3$ pretreated with D_2O (see the Supporting Information), the deuterium was introduced at the 3-position of **3aa**, and the content was 78% [Eq. (5)]. Therefore, the hydrogen at the 3-position of **3aa** mainly comes from water (or proton) on the catalyst.[19] The results of the deuterium-labeling experiments are consistent with the above-mentioned possible mechanism involving the acetylide formation (via cleavage of the terminal C–H bond) and the ligand exchange between the vinyl copper intermediate and water (or proton).





In conclusion, $Cu(OH)_x/Al_2O_3$ could act as an efficient heterogeneous catalyst for the 1,3-dipolar cycloaddition reaction of azomethine imines to terminal alkynes. The observed catalysis was intrinsically heterogeneous, and the catalyst was reusable without significant loss of its catalytic activity. The in situ generated copper(I) species is the catalytically active species for the present cycloaddition. The present systems have the following significant advantages; 1) applicability to various dipoles and dipolarophiles, 2) much higher catalytic activities than those of the previously reported heterogeneous catalyst,[9] 3) no use of stabilizing ligands, 4) easy catalyst/product separation, and 5) reusability of the $Cu(OH)_x/Al_2O_3$ catalyst.

Experimental Section

The supported copper hydroxide $Cu(OH)_x/Al_2O_3$ was prepared according to the literature procedure.[11] The aqueous solution (60 mL) of $CuCl_2·2H_2O$ (0.085 g, 8.3 mM) containing the Al_2O_3 powder (2.0 g) calcined at 550 °C was vigorously stirred at room temperature. After 15 min, the pH of the solution was quickly adjusted to 12 by addition of an aqueous solution of NaOH (1.0 M, base treatment), and the resulting slurry was further stirred for 24 h. The solid was then filtered off, washed with a large amount of water, and dried in vacuo to afford $Cu(OH)_x/Al_2O_3$ (2.0 g) as a light blue powder. This powder contained 1.6 wt % copper and approximately 10 wt % water. The XRD pattern of $Cu(OH)_x/Al_2O_3$ was the same as that of the parent Al_2O_3 support and no signals due to copper metal (clusters) and copper oxides were observed. The XPS spectrum of $Cu(OH)_x/Al_2O_3$ showed the binding energies of Cu $2p_{3/2}$ at 933.8 eV (full width at the half maximum: 3.7 eV) with the shakeup satellite peak at 942.3 eV, suggesting that the oxidation state of the copper species is +2.[20] No chlorine was detected in $Cu(OH)_x/Al_2O_3$ by the XPS measurement. In the radial distribution functions from the Fourier transformation of the k^3-weighed EXAFS for $Cu(OH)_x/Al_2O_3$, the signals due to Cu–O–Cu and Cu–Cu shells were hardly observed. The absence of these shell signals suggests that no networks of linked copper species exist in $Cu(OH)_x/Al_2O_3$. All these results suggest that copper(II) hydroxide is highly dispersed on Al_2O_3.

The 1,3-dipolar cycloaddition was carried out as follows. Into a glass vial were successively placed $Cu(OH)_x/Al_2O_3$ (Cu: 1.5 mol % with respect to an azomethine imine), an azomethine imine (0.5 mmol), an alkyne (0.55 mmol), and a solvent (2 mL). Then, the resulting solution was stirred at 40 °C under an Ar atmosphere. The yields were determined by ^1H NMR analysis. After the reaction was completed, $Cu(OH)_x/Al_2O_3$ was separated by filtration and was further washed with toluene. The filtrate was passed through a short silica gel column, and then evaporated in vacuo to give **3aa** (93 % isolated yield). The retrieved $Cu(OH)_x/Al_2O_3$ was washed with toluene and dried in vacuo before recycling. The products were confirmed by the comparison of their NMR spectra with those of authentic data.[7–9]

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Keywords: alkynes · azomethine imines · copper hydroxide · heterogeneous catalysis · *N,N*-bicyclic pyrazolidinone

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[10] The development of easily recoverable and recyclable heterogeneous catalysts by filtration or centrifugation can solve the problems of the homogeneous systems and has received particular interest for the synthesis of fine chemicals: R. A. Sheldon, H. van Bekkum, *Fine Chemical through Heterogeneous Catalysis*, Wiley, Weinheim, **2001**.

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[14] Compound **4aa**: MS (EI): m/z (%): 194 (1.2) [M^+], 150 (40), 149 (85), 148 (23), 106 (43), 105 (17), 104 (18), 78 (17), 77 (100), 76 (27), 51 (11).

[15] The treatment of a [D$_8$]toluene solution of **2a′** (D content at the terminal position: 94 %, 0.27 M, 2 mL) with $Cu(OH)_x/Al_2O_3$ (Cu: 1.4 mol % with respect to **2a′**) at 20 °C for 1 h resulted in a decrease in the deuterium content from 94 % to 42 %. Also, Al_2O_3 took part in the H/D exchange reactions. Thus, the H/D exchange readily takes place on $Cu(OH)_x/Al_2O_3$.

[16] In the UV/Vis spectrum of copper(I) phenyl acetylide $[Cu^I(C{\equiv}CPh)]_n$, a similar broad absorption band was observed around 400–460 nm.[11c]

[17] The 1,3-dipolar cycloaddition of **1a** to ethyl 2-butynoate (internal alkyne) under the conditions described in Table 2 did not proceed,

also suggesting that the copper species in $Cu(OH)_x/Al_2O_3$ is terminally bound to an alkyne to form the copper acetylide species.

[18] Compound **2a′** was synthesized according to the literature procedure: T. Schwier, V. Gevorgyan, *Org. Lett.* **2005**, *7*, 5191–5194.

[19] It was confirmed that no H/D exchange reaction of the hydrogen at the 3-position of non-deuterated **3aa** proceeded in the presence of $Cu(OH)_x/Al_2O_3$ pretreated with D_2O.

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