## ChemComm



## COMMUNICATION

**View Article Online** 



Cite this: Chem. Commun., 2016 52 6549

Received 8th March 2016, Accepted 12th April 2016

DOI: 10.1039/c6cc02063a

www.rsc.org/chemcomm

## Catalytic transformation of esters of 1,2-azido alcohols into α-amido ketones†

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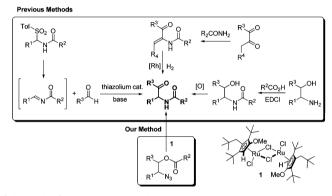
The esters of 1,2-azido alcohols were transformed into  $\alpha$ -amido ketones without external oxidants through the Ru-catalyzed formation of N-H imines with the liberation of N2 followed by intramolecular migration of the acyl moiety. A wide range of  $\alpha$ -amido ketones were obtained, and one-pot transformation into the corresponding oxazoles (or a thiazole) was demonstrated.

α-Amido ketones are biologically relevant molecules and useful building blocks for valuable compounds in organic synthesis.<sup>1</sup> In addition, they are useful substrates in various organic transformations such as the Robinson-Gabriel reaction to oxazoles<sup>2</sup> and thiazoles, 2e the Norrish-Yang photocyclization to 2-aminocyclobutanols,3 the epoxy-annulation reaction to epoxide-fused heterocycles<sup>4</sup> and the reaction with ammonium acetate (or primary amines) to imidazoles.<sup>5</sup>

For the versatile transformations,  $\alpha$ -amido ketones have been synthesized by various methods, including Pd-catalyzed coupling reaction of methylene aziridines with carboxylic acids,6 Rh-catalyzed denitrogenative hydration of N-sulfonyl-1,2,3-triazoles,<sup>7</sup> the Dakin-West reaction of α-amino acids with acid anhydrides, 8 the Neber rearrangement of ketoxime sulfonates<sup>9</sup> and a radical cascade reaction of alkynes with N-fluoroarylsulfonimides and alcohols.<sup>10</sup> However these methods suffer from the difficulty in preparing substrates, harsh reaction conditions, and/or limitations of the substrate scope.

Additional and noticeable methods are compared with our new finding in Scheme 1. The aza-benzoin condensation reaction of aldehydes with N-acyl imines is an interesting method using thiazolium organocatalysts. 5c,11 However, the synthesis of tosylamides from tosylsulfinic acid, amides, and aldehydes is required to generate the intermediate N-acyl imines, and is not effective for enolizable aldehydes. 12 The asymmetric hydrogenation of α-dehydroamido ketones can provide optically active α-amido ketones, 13 but the scope is limited by the intrinsic

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Scheme 1 Synthetic methods for  $\alpha$ -amido ketones.

regioselectivity problem in the condensation reaction of 1,2-diketones and primary amides. An old method employing 1,2-amino alcohols as the starting substrates looks simple but suffers practically from inefficiency in the N-acylation and the subsequent oxidation.5c,14 A carboxyl-activating agent and an oxidant are required in a stoichiometric amount in the acylation and the oxidation, respectively. Meanwhile, 1,2-amino alcohols are frequently prepared from 1,2-azido alcohols by the Staudinger reaction using triphenylphosphine as a reductant. Herein we wish to report an efficient synthesis of α-amido ketones from 1,2-azido alcohols without oxidation and reduction steps through a novel one-step catalytic transformation of 1,2-azido esters under neutral and mild conditions.

Recently we found an interesting Ru-catalyzed transformation of alkyl azides to N-H imines. 15 As an application of the catalytic transformation, we have developed an efficient method for the synthesis of enamides from alkyl azides and acyl donors utilizing the N-acylation of intermediate N-H imines. 16 In a related study on the N-acylation of N-H imines containing a hydroxyl group, we observed the unexpected formation of  $\alpha$ -amido ketones in the catalytic reactions of 1,2-azido alcohols. For example, N-(2-oxo-1,2-diphenylethyl)acetamide (3a) was obtained in 55% yield by the reaction of 2-azido-1,2-diphenylethanol with acetic anhydride in the presence of the ruthenium catalyst 1 (Scheme 2). Then we envisioned

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Scheme 2 Formation of  $\alpha$ -amido ketone 3a from 1,2-azido acetate 2a or from the corresponding 1,2-azido alcohol.

that its intramolecular version would improve the efficiency of the transformation. We examined the transformation of 2-azido-1,2-diphenylethyl acetate (2a) under various conditions (Table 1). The transformation was more efficient in polar solvents than in non-polar ones such as THF and toluene (entries 1 and 2). In dimethylformamide (DMF), 3a was formed in 89% yield (entry 3). Noticeably, the transformation was effective in ionic liquids, <sup>17</sup> which have some advantages such as being experimentally safe and recycled. In particular 3a was formed in almost quantitative vield in 1-butyl-3-methylimidazolium chloride ([bmim]Cl) (entry 4). A gram-scale reaction was also effective to give 3a in 91% isolated yield (entry 5), and recycling of [bmim]Cl was possible simply by removing water from the aqueous phase by heating after the workup procedure (entry 6). 18 Decreasing the reaction temperature to 50 °C significantly lowered the yield of 3a (entry 7), while increasing it to 100 °C was not beneficial (entry 8). As in the synthesis of enamides involving N-acylation of N-H imines, 16 a catalytic amount of triethylamine was helpful for the formation of 3a (entry 9).17

The transformation to  $\alpha$ -amido ketones was applicable for a broad range of acetates of 1,2-azido alcohols (Table 2). The electronic effect of the substituents of aromatic rings was not so

Table 1 Transformation of 2a to 3a under various conditions<sup>a</sup>

	Ph OAc Ph	1 (1.0 mol%)  solvent Additive (2.0 mol%) Temperature  NHAc Ph O Ph 3a		
Entry	Solvent	Additive	Temp. (°C)	Yield <sup>b</sup> (%)
1	THF	Et <sub>3</sub> N	70	15
2	Toluene	$Et_3N$	70	28
3	DMF	$Et_3N$	70	89

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1	THF	Et <sub>3</sub> N	70	15
2	Toluene	$Et_3N$	70	28
3	DMF	$Et_3N$	70	89
4	[bmim]Cl	$Et_3N$	70	$96 (94)^c$ $91^{c,d}$
5	[bmim]Cl	$Et_3N$	70	
6	[bmim]Cl	$Et_3N$	70	$90^e$
7	[bmim]Cl	$Et_3N$	50	15
8	[bmim]Cl	$Et_3N$	100	91
9	[bmim]Cl	None	70	85

<sup>&</sup>lt;sup>a</sup> Typical reaction conditions: a solution of an azide (0.25 mmol), 1 (1.0 mol%) and  $\rm Et_3N$  (2.0 mol%) in a solvent (1.0 mL) was stirred for 12 h.  $^b$  Estimated by  $^1$ H NMR using nitromethane as an internal standard.  $^c$  Isolated yield.  $^d$  A large scale reaction employing 1.06 g (3.6 mmol) of 2a and 15 mg (0.5 mol%) of 1 in 6.0 mL of [bmim]Cl at 70 °C for 36 h. <sup>e</sup> The yield of the reaction using [bmim]Cl recovered from the 5th recycling reaction.

significant (3a-3c and 3g-3h). The yields of α-amido ketones were high in the transformation of the derivatives having alkyl groups (3d-3i). The low yield of 3i was due to the formation of unidentified side-products, and the use of DMF as a solvent gave 3i in 62% yield. The transformation of esters of primary β-hydroxy azides to α-amido ketones (3k-3r) was also successful despite the fact that the intermediates are unstable N-H aldimines. The transformation was effective for various derivatives containing functional groups on aromatic rings such as methyl, methoxy, halides and nitrile substituents. The yield of the  $\alpha$ -amido ketone (3s), which has a benzyl moiety, was moderate with the formation of unidentified side products. The transformation of cyclic substrates (3t-3w) was less efficient than that of linear ones, probably due to the rigidity of ring structures. A six-membered cyclic  $\alpha$ -amido ketone (3**u**) was obtained in moderate yield, while a five-membered one (3t) was not formed. However, interestingly, a seven-membered cyclic one (3w) was obtained in high yield, and a benzofused six-membered bicyclic one (3v) was formed in a much higher yield than the monocyclic one (3u).

Then, the scope of  $\alpha$ -amido ketones was explored for the derivatives having various N-acyl groups (Table 3). R3 in the α-amido ketones 5 could be varied not only to an ethyl (5a), isopropyl (5b), or a tert-butyl (5c) group but also to a conjugated alkenyl (5d), chloromethyl (5e), or an ester (5f) group. The derivatives containing phenyl (5g), furyl (5h), and thiofuryl (5i)

**Table 2** Synthesis of  $\alpha$ -amido ketones from 1,2-azido acetates<sup>a</sup>

3v: 81%[e]

**3u**: 58%<sup>[d]</sup>

<sup>&</sup>lt;sup>a</sup> Standard reaction conditions: a solution of an azide 2 (0.25 mmol), 1 (1.0 mol%) and Et<sub>3</sub>N (2.0 mol%) in [bmim]Cl (1.0 mL) was stirred for 12 h. <sup>b</sup> Reaction was carried out in DMF. <sup>c</sup> Not detected. <sup>d</sup> Reaction was carried out for 24 h. e Reaction was carried out for 36 h.

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**Table 3** Synthesis of  $\alpha$ -amido ketones from various esters of 1.2-azido alcohols<sup>a</sup>

<sup>a</sup> Standard reaction conditions: a solution of an azide 4 (0.25 mmol), 1 (1.0 mol%) and Et<sub>3</sub>N (2.0 mol%) in [bmim]Cl (1.0 mL) was stirred for 12 h. b Reaction was carried out in DMF for 36 h at 100 °C.

groups were also obtained in high yields. The migration of the butyloxycarbonyl (Boc) group was possible, although heating at a higher temperature for a longer reaction time was required to give an N-Boc protected derivative (5i) in good yield.

To demonstrate the utility of our synthesis of α-amido ketones, we carried out one-pot transformations to oxazoles (6a-c) and a thiazole (7) (Scheme 3). Treatment of 3a in situ generated from 2a with sulfuric acid afforded oxazole 6a in 94% yield. The corresponding thiazole (7) was obtained by the treatment with Lawesson's reagent in 87% yield. Noticeably, oxaprozin (6b), which is a well-known non-steroidal anti-inflammatory drug,<sup>19</sup> was obtained directly from 4f in 89% yield. The stereochemistry of 4k at the  $\alpha$ -position was practically maintained during the one-pot transformation to  $6c_1^{20}$  although the intermediate α-amido ketone was formed as a 1:1 diastereomeric mixture.

To obtain mechanistic insights into the transformation of 1,2-azido esters to α-amido ketones, a crossover experiment and the generation of an enol amide were examined: only non-crossover

Scheme 3 One-pot transformations to oxazoles and a thiazole.

Mechanistic investigation. Scheme 4

$$\begin{bmatrix} R^3 & O & R^2 & \mathbf{1} \\ R^1 & N_3 & O & \mathbf{R}^2 \\ \mathbf{R}^1 & N_4 & \mathbf{R}^2 \end{bmatrix} \begin{bmatrix} R^3 & O & R^2 \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} O & O & \mathbf{R}^3 & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{R}^2 \end{bmatrix} \xrightarrow{R^3} \begin{bmatrix} R^3 & O & O \\ R^1 & N & \mathbf{$$

Scheme 5 Plausible pathway for the formation of  $\alpha$ -amido ketones.

products (3a and 9) were formed in high yields in the transformation of a mixture of the 1,2-azido acetate 2a and another azide (8) containing a benzoyl group (Scheme 4a), and the α-amido ketone 3a was obtained in 76% yield in the deprotection reaction of a MOM-protected enol amide (10) (Scheme 4b).<sup>21</sup>

Now we can propose a plausible pathway for the transformation of the esters of 1,2-azido alcohols into  $\alpha$ -amido ketones (Scheme 5). On the basis of our previous reports on the formation of enamides from N-acyl imines, 16 the results of the crossover experiment support intramolecular migration of the acyl group in the intermediate N-H imine **A** to give the  $\alpha$ -hydroxyl N-acylimine **B**. And the result of the deprotection reaction of 10 is indicative of the intermediacy of the enol amide C, which is tautomerized to the final  $\alpha$ -amido ketone product.

In summary, we developed a new and simple method for the synthesis of  $\alpha$ -amido ketones from the esters of 1,2-azido alcohols just by the liberation of molecular nitrogen under mild conditions. Our method is effective for the synthesis of a wide range of multi-substituted α-amido ketones, and efficient for gram scale synthesis in recyclable ionic liquids. In addition, we demonstrated the one-pot synthesis of oxazoles and a thiazole using α-amido ketones as intermediates.

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (2015R1A2A2A01008130).

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