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Copper-Catalyzed Cyclization and Azidation of γ,δ-Unsaturated Ketone O-Benzoyl Oximes

Hailin Su,[a] Weifei Li,[a] Zhaoli Xuan,[a] and Wei Yu[a,*]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People's Republic of China
Fax: (+86)-931-891-2582; e-mail: yuwei@lzu.edu.cn

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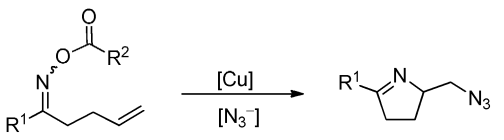
Abstract: An intramolecular imination/azidation sequence has been realized through the tetrakis(acetonitrile)copper(I) hexafluorophosphate [$Cu(CH_3CN)_4PF_6$]-catalyzed reaction of γ,δ-unsaturated ketone *O*-benzoyl oximes with trimethylsilyl azide ($TMSN_3$). The reaction proceeds *via* the copper-mediated N–O cleavage and subsequent C–N forming 5-*exo* cyclization. The thus formed intermediate is then azidated to afford the corresponding dihydropyrrole product. Preliminary mechanistic investigations suggest that the cyclization step does not involve a radical intermediate.

Keywords: azidation; copper catalysis; cyclization; dihydropyrroles; γ,δ-unsaturated *O*-benzoyl ketoximes

Olefin diamination reactions have received much attention from organic chemists due to the importance of 1,2-diamine-bearing compounds.[1] As a result, significant progress has been made recently in this aspect with the development of new transition metal-catalyzed proc[2] When the olefin diamination is realized in an intramolecular manner by tethering one (or two) nitrogen atom(s) with the alkene moiety, functionalized nitrogen heterocycles will be furnished. As such, several important methodologies employing palladium,[3] nickel,[4] gold,[5] and copper[6] as catalyst have been developed for this purpose. However, these studies mainly deal with unsaturated amide or sulfonamide derivatives, whereas reactions involving other types of nitrogen sources have much less been explored.

Oxime derivatives can be cleaved at the N–O bond by the action of transition metals to form active iminyl intermediates, which can be tailored to form new C–N bonds.[7] Copper salts are effective catalysts to promote the reductive N–O bond cleavage of *O*-acyl oximes and subsequent C–N bond formation, and this imination strategy has recently found wide applications in the synthesis of nitrogen heterocycles.[8,9] The use of copper(I) salts toward this goal was first reported by Narasaka et al.[10] These researchers found that $CuBr{\cdot}SMe_2$ could effectively catalyze the cyclization of γ,δ-unsaturated ketone *O*-alkoxycarbonyl or *O*-pentafluorobenzoyl oximes to afford dihydropyrrole products.[10a] When the reaction was performed in the presence of an excess amount of $LiBr{\cdot}H_2O$, 2-bromomethyldihydropyrrole products were obtained in high yields. Inspired by this work, we envisioned that by using nucleophilic azides as the nitrogen source, the azidyl group would be introduced onto the alkene moiety after cyclization.[11–13] Thus, an intramolecular imination/azidation sequence could be realized (Scheme 1). As the azidyl group is synthetically versatile,[11] the thus formed dihydropyrrole products could serve as precursors for other useful compounds in organic synthesis.

To achieve this goal, we initiated the study by choosing $TMSN_3$ and NaN_3 as the azidation agents, and several low-valent copper species such as $CuBr{\cdot}SMe_2$, $Cu(CH_3CN)_4PF_6$ (shorten as $CuPF_6$ below), Cu powder and Cu_2O as catalyst to promote the reaction of (*E*)-1-phenylpent-4-en-1-one *O*-benzoyl oxime (**1a**).[14] Preliminary results showed that when $TMSN_3$ was used as the azide source, the desired reaction could happen, but NaN_3 was invalid under the same conditions. $CuPF_6$ was the most effective catalyst among these copper species. When **1a**



Scheme 1. Expected intramolecular imination/azidation of γ,δ-unsaturated *O*-acyl oximes

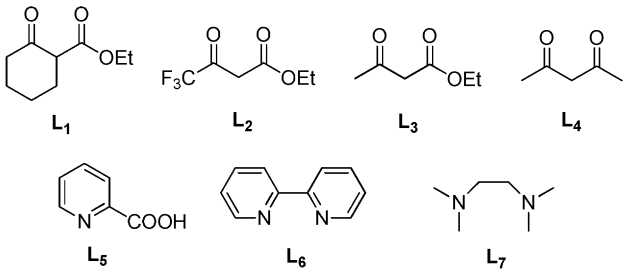


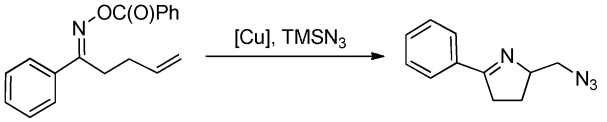
Figure 1. Structure of ligands $\mathbf{L_1}$–$\mathbf{L_7}$.

was treated with 3.0 equiv. of $TMSN_3$ and 0.2 equiv. of $CuPF_6$ in 1,2-dichloroethane (DCE) at 80 °C, the desired product **2a** was obtained in a yield of 54%. Using other solvents such as toluene, dichloromethane (DCM), 1,4-dioxane, acetonitrile and dimethoxyethane (DME) delivered inferior results. To further improve the yield of **2a**, we evaluated the effect of several common copper ligands including 1,3-dicarbonyl compounds $\mathbf{L_1}$, $\mathbf{L_2}$, $\mathbf{L_3}$ and $\mathbf{L_4}$, picolinic acid ($\mathbf{L_5}$), 2,2′-bipyridine ($\mathbf{L_6}$) and TMEDA ($\mathbf{L_7}$) (Figure 1). It was found that the yield of **2a** could be enhanced by using 0.2 equiv. of $\mathbf{L_1}$ together with 0.2 equiv. of $CuPF_6$ (Table 1, entry 5). The yield was somewhat lower when smaller amounts of $TMSN_3$ were used. Other ligands were less effective in comparison with $\mathbf{L_1}$. The representative screening experiments are summarized in Table 1.

The optimized conditions (Table 1, entry 5) were then applied to a variety of γ,δ-unsaturated *O*-benzoyl oxime derivatives **1b–1u**, and the results are listed in Table 2. In general, the cyclization products were obtained in moderate to good yields. For 1-aryl-substituted oxime derivatives, the yield was lower when the aryl ring was an electron-rich furan or thiophene (entries 5 and 6). Better results were obtained when the substrates were disubstituted with methyl groups at the α-position (entries 12–19), which reflects the favorable Thorpe–Ingold effect. On the other hand, if the α-carbon is tertiary, the azidation will take place at the α-position as well (entries 8, 9 and 20). The products **3h**, **3i** and **3t** were isolated from the reaction mixture as single isomers. It is also interesting to see that for substrates **1k**, **1n** and **1s**, the reaction delivered olefination product **4** as well as azidation product **2** (entries 11, 14, 19). The olefination products like **4** are generally formed from the palladium-catalyzed cyclization of γ,δ-unsaturated ketone pentafluorobenzoyl oximes.[7a,b,15] When compounds **1p** and **1q** (entries 16 and 17) were subjected to the present conditions, the benzoyloxy transfer products **5p** and **5q** were also generated, respectively, besides **2p** and **2q**.

The Cu(I)-catalyzed and *O*-acyl oxime-involved C–N bond forming reactions are interesting from the mechanistic point of view. The reaction might initially generate iminyl radicals,[10,15d,16,17] or proceed *via* the

Table 1. Screening of conditions for the reaction of **1a**.[a]



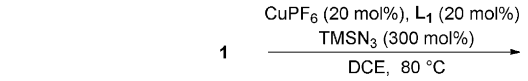
1a 2a

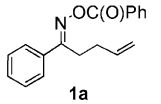
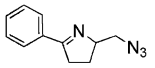
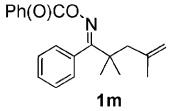
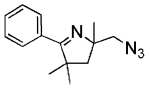
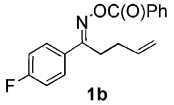
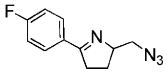
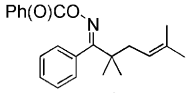
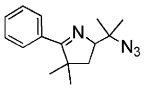
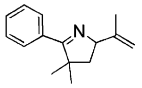
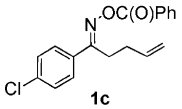
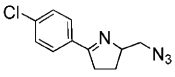
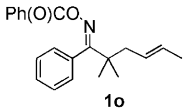
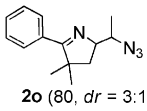
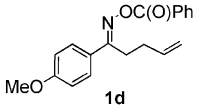
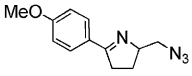
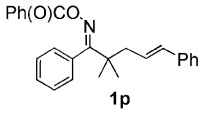
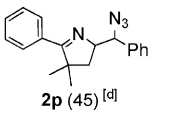
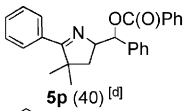
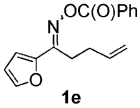
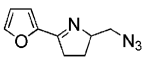
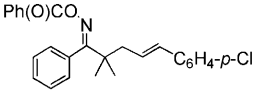
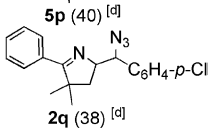
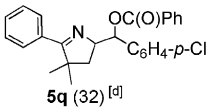
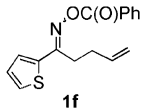
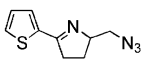
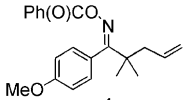
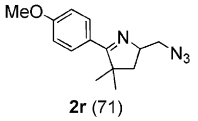
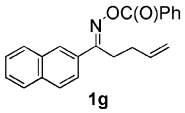
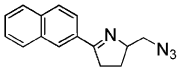
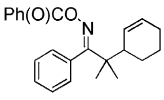
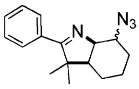
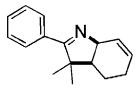
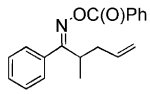
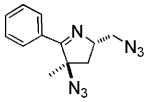
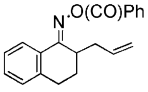
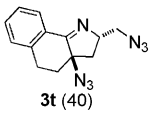
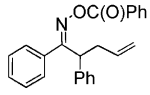
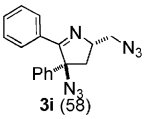
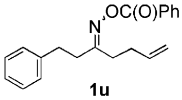
Entry	Copper (equiv.)	Additive	Solvent	Yield of **2a** [%][b]
1	$CuPF_6$ (0.2)	none	DCE	54
2	Cu_2O (0.2)	none	DCE	23
3	Cu (0.2)	none	DCE	13
4	CuBr (0.2)	none	DCE	24
5	***$CuPF_6$ (0.2)***	***L_1 (0.2)***	***DCE***	***66***
6	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	DCE	47[c]
7	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	DCE	58[d]
8	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.4)	DCE	58
9	$CuPF_6$ (0.1)	$\mathbf{L_1}$ (0.2)	DCE	42
10	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	DCE[e]	34
11	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	DCE[f]	53
12	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	DCE[g]	50
13	$CuPF_6$ (0.2)	$\mathbf{L_2}$ (0.2)	DCE	60
14	$CuPF_6$ (0.2)	$\mathbf{L_3}$ (0.2)	DCE	55
15	$CuPF_6$ (0.2)	$\mathbf{L_4}$ (0.2)	DCE	53
16	$CuPF_6$ (0.2)	$\mathbf{L_5}$ (0.2)	DCE	58
17	$CuPF_6$ (0.2)	$\mathbf{L_6}$ (0.2)	DCE	40
18	$CuPF_6$ (0.2)	$\mathbf{L_7}$ (0.2)	DCE	37
19	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	DCM	10
20	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	toluene	50
21	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	acetonitrile	–[h]
22	$CuPF_6$ (0.2)	$\mathbf{L_1}$ (0.2)	1,4-dioxane	–[h]

[a] The reaction was performed in a 0.05 M solution of **1a** and 3.0 equiv. of $TMSN_3$ contained in a sealed tube at 80 °C unless otherwise specified. Compound **1a** has the *E* configuration.[14] DCE = dichloroethane; DCM = dichloromethane.
[b] Isolated yield.
[c] 1.0 equiv. of $TMSN_3$ was used.
[d] 2.0 equiv. of $TMSN_3$ were used.
[e] At room temperature.
[f] At 50 °C.
[g] At 100 °C.
[h] Starting material decomposed.

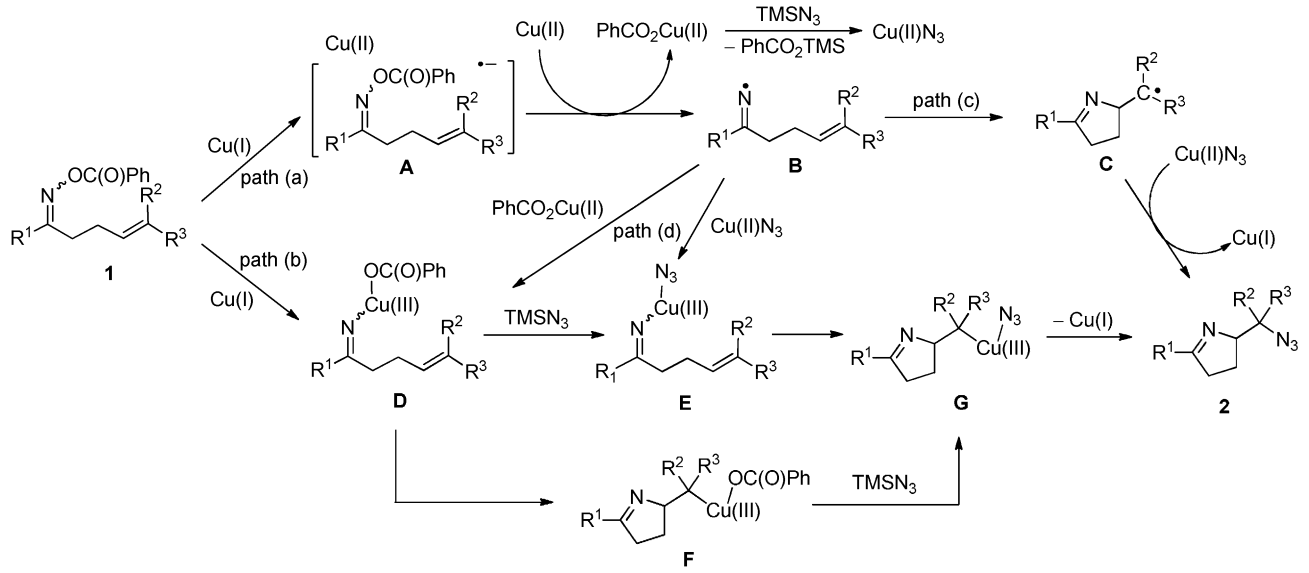
oxidative addition of Cu(I) to the N–O bond.[8] In the present cases, two mechanisms can be proposed according to the indicated literature to account for the formation of **2**. They are illustrated in Scheme 2. In the first mechanism, the reaction is initiated by single electron transfer (SET) between **1** and Cu(I), followed by the N–O cleavage to deliver iminyl radical **B** [path (a)] The latter is then converted to carbon radical **C** in the cyclization step [path (c)]. In the SET step, Cu(I) is oxidized to Cu(II), which takes the form of $Cu(II)N_3$ in the presence of $TMSN_3$. The oxidation of **C** by $Cu(II)N_3$ finally gives **2**. Alternatively, as indicated by path (b), the first step involves the oxidative addition of Cu(I) to the N–O bond in **1**, resulting in the formation of intermediate **D**. After ligand ex-

Table 2. Copper-catalyzed cyclization of compounds **1**.[a]

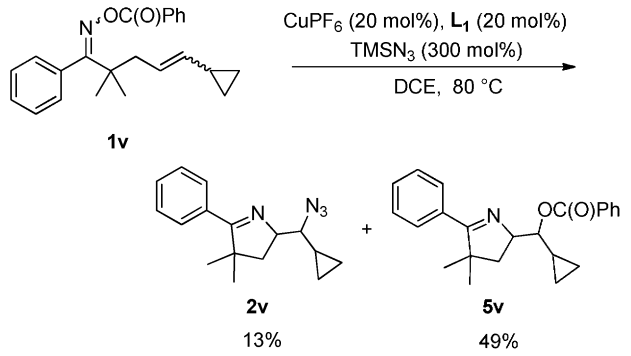


Entry	Substrate **1**	Product(s) (Yield [%]) [b]	Entry	Substrate **1**	Product(s) (Yield [%]) [b]
1	 **1a**	 **2a** (66)	13	 **1m**	 **2m** (75)
2	 **1b**	 **2b** (64)	14	 **1n**	 **2n** (17)  **4n** (80)
3	 **1c**	 **2c** (62)	15	 **1o**	 **2o** (80, *dr* = 3:1) [c]
4	 **1d**	 **2d** (60)	16	 **1p**	 **2p** (45) [d]  **5p** (40) [d]
5	 **1e**	 **2e** (57)	17	 **1q**	 **2q** (38) [d]  **5q** (32) [d]
6	 **1f**	 **2f** (43)	18	 **1r**	 **2r** (71)
7	 **1g**	 **2g** (65)	19	 **1s**	 **2s** (38, *cis*/*trans* = 1.3)  **4s** (48)
8	 **1h**	 **3h** (54)	20	 **1t**	 **3t** (40)
9	 **1i**	 **3i** (58)	21	 **1u**	**2u** (45)
10	**1j**	**2j** (43)			
11	**1k**	**2k** (22) **4k** (70)			
12	**1l**	**2l** (86)			

[a] The reaction was performed on a 0.5 mmol scale.
[b] Isolated yield.
[c] Relative configuration was undetermined.
[d] The product was isolated as a single isomer, but its relative configuration was undetermined.



Scheme 2. Proposed reaction mechanism for the formation of **2**.



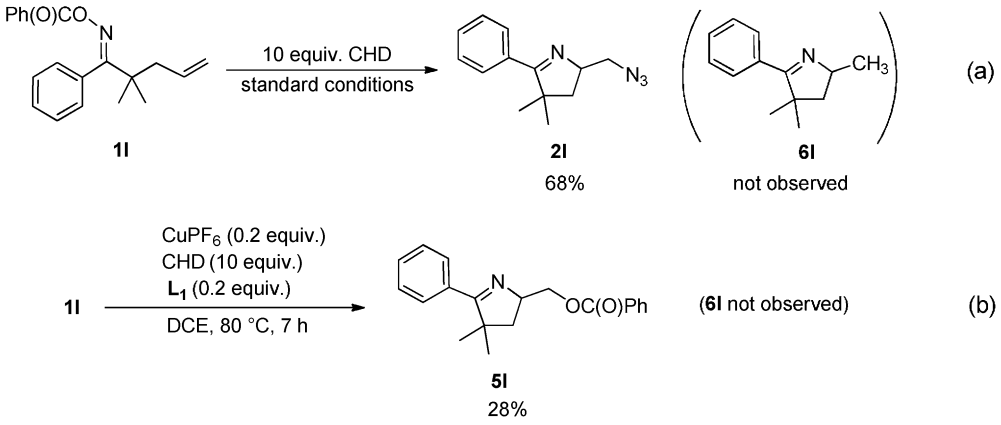
Scheme 3. The radical clock experiment with compound **1v**.

change between $PhCO_2^-$ and N_3^- (from **D** to **E**) and subsequent cyclization (and/or through an alternative sequence of **D** to **F** to **G**), **G** is produced, which then undergoes reductive elimination to afford **2**. A similar organic Cu(III) species has been proposed for the copper-catalyzed intermolecular olefin aminoacetoxylation by Blakey et al.[18] It is also possible that **D** or **E** is generated through the binding of iminyl radical **B** with Cu(II) [path (d)]. At the current stage, however, these two pathways [path (b) and path (d)] cannot be distinguished. Compounds **4**, as generated in the reaction of **1k**, **1n** and **1s**, might as well derived directly from intermediates **G** and **F**.

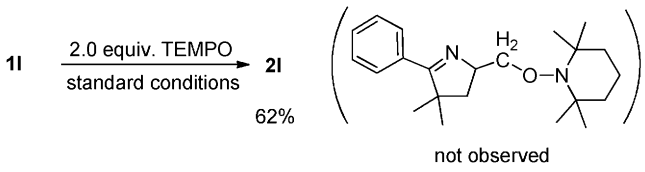
To shed light on the reaction mechanism, compound **1v** was prepared and treated with $CuPF_6$ under the indicated reaction conditions (Scheme 3). We assumed that if the reaction followed the radical process represented by path (a) and (c), ring-opening products would be obtained.[19,20] However, as the experiment demonstrated, **1v** was mainly converted to compounds **2v** and **5v**, and only tiny amounts of ring-opening products were detected after reaction (<5%). This result suggests that the cyclization step is less likely a free radical process. Thus, we believe that path (b) represents a more reasonable mechanism for the present reaction. Ligand $\mathbf{L_1}$ might help to stabilize the Cu(III) species as the yields of products **2** were lower in the absence of it (Table 1, entry 1).

Besides this experiment, we also investigated the reaction of **1l** in the presence of 1,4-cyclohexadiene (CHD) and 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO) (Scheme 4 and Scheme 5). It was expected that if the cyclization involved generation of carbon radical **C**, reduction product **6l** would be obtained when CHD was present in the reaction system;[10a,16] and **C** could also be captured by TEMPO. However, our result showed that when the reaction was performed with 10 equiv. of CHD under otherwise the same conditions, only compound **2l** was generated in a yield of 68% [Scheme 4, (a)]; no **6l** was obtained even in the absence of $TMSN_3$ [Scheme 4, (b)]. In the latter case, **5l** was formed in a yield of 28%. The experiment with TEMPO also failed to capture radical intermediate **C** (Scheme 5).

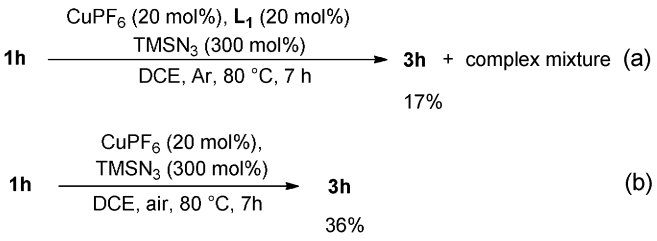
As shown in Table 2, for substrates bearing an internal aryl-substituted alkene unit such as **1p** and **1q**, the reaction afforded **5p** and **5q** apart from the corresponding azidation products. This phenomenon can also be accounted for with the reaction mechanism shown in Scheme 2. We think that the carbons bound exocyclic to copper in intermediate **F** and **G** are of carbocationic character in the subsequent product-forming reductive elimination step, and this process would be facilitated by the benzene ring attached to



Scheme 4. Reaction of **1l** in the presence of CHD.



Scheme 5. Reaction of **1l** in the presence of TEMPO.

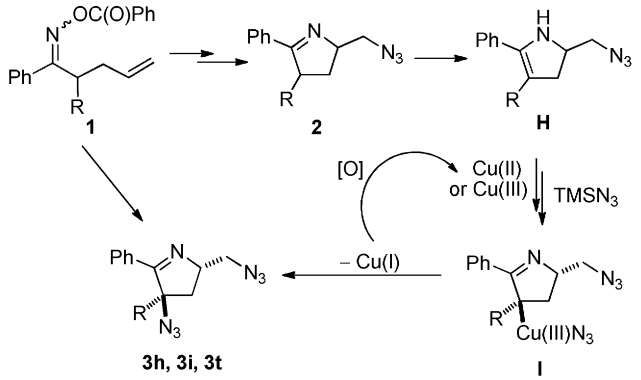


Scheme 6. Control experiments with **1h**.

it. Therefore, in the cases of **1p** and **1q**, the reductive elimination at the stage of **F** became competitive with ligand exchange with N_3^-, and thus **5p** and **5q** were formed. The findings that, in the reaction of **1v**, **5v** becames the major product is also consistent with this hypothesis: the cyclopropyl group can be a stronger carbocation-stabilizing group than the benzene ring,[21] so the ligand coupling of **F** during the reaction of **1v** was more favored. Furthermore, this result suggests that process from **D** to **G** shown in Scheme 2 probably would pass through intermediate **F**.

When **1h**, **1i** and **1t** were used as the substrate, the reactions yielded **3h**, **3i** and **3t**, respectively. This result is surprising because the introduction of the second azido group at the α-position requires an oxidative process. Although the mechanism of this second azidation is still unclear, we believe that the active oxidant in this system is the Cu(II) or Cu(III) species, which, as suggested in Scheme 2, are generated *in situ* during the reaction. However, as $CuPF_6$ was used in only 0.2 equiv., apparently another stoichiometric oxidant is required. Our reactions were performed in a sealed tube, which was not pre-deaerated before heating.[22] It is possible the air present in the reaction tube played the role of terminal oxidant to recycle the Cu(II) or Cu(III) species. To test this hypothesis, we did control experiment with **1h** by bubbling the DCE solvent with argon for 15 min. before reaction. Still, compound **3h** was obtained after reaction, but the yield was much lower [Scheme 6, (a)]. Apart from **3h**, no other product could be isolated in pure form and structurally identified. Probably, in the absence of oxygen, **1h** itself would act as oxidant to recycle the copper. The fact that only **1h**, **1i** and **1t** can be transformed to compounds **3** indicates that the presence of a substituent at the α position is a prerequisite for the α-azidation to take place. Our control experiment also showed that ligand $\mathbf{L_1}$ had a beneficial effect on this reaction; the yield decreased to some extent in the absence of it [Scheme 6, (b)]. A tentative mechanism is proposed in Scheme 7 to account for the formation of **4**.

In summary, we have demonstrated that by using $TMSN_3$ as the azidating agent, the Cu(I)-catalyzed cyclization of γ,δ-unsaturated ketone *O*-benzoyl oxime derivatives can be achieved in an intramolecu-



Scheme 7. Proposed mechanism for the formation of **3h**, **3i** and **3t**.

lar imination/azidation pattern, affording the azide-functionalized dihydropyrrole products in moderate to good yields. There is evidence to suggest that the cyclization step does not involve a radical intermediate. Further investigation is being done in this laboratory with an aim to develop an enantioselective version of this reaction.

Experimental Section

General Experimental Procedure for the Copper-Catalyzed Reaction of 1

A suspension of γ,δ-unsaturated *O*-benzoyl ketoximes **1** (0.5 mmol, 1.0 equiv.), $CuPF_6(CH_3CN)_4$ (37 mg, 0.1 mmol, 0.2 equiv.), $TMSN_3$(173 mg, 1.50 mmol, 3.0 equiv.), and $\mathbf{L_1}$ (ethyl 2-oxocyclohexanecarboxylate) (17 mg, 0.1 mmol) in 1,2-dichloroethane (10 mL) was stirred at 80 °C (oil bath temperature). After the reaction was complete (in 7 h) as monitored by TLC, the mixture was cooled to 20 °C, and then quenched with a saturated aqueous solution of Na_2CO_3 (15 mL). The organic and the aqueous layers were separated, and the latter was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layers were washed sequentially with a saturated aqueous solution of Na_2CO_3 (15 mL × 3) and water (15 mL × 3). The organic phase was dried over Na_2SO_4, filtered and the filtrate was evaporated under reduced pressure with a rotatory evaporator. The residue was purified by column chromatography to give **2** and (others).

Acknowledgements

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