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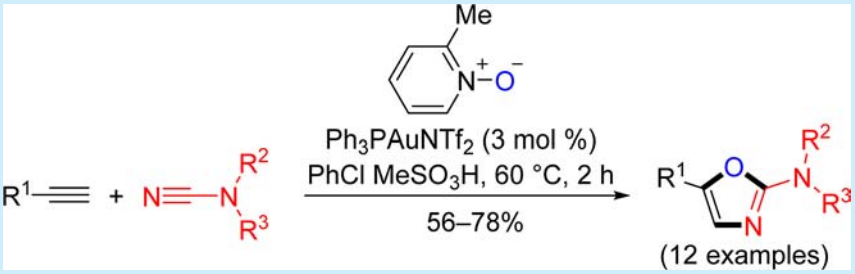
Facile Gold-Catalyzed Heterocyclization of Terminal Alkynes and Cyanamides Leading to Substituted 2-Amino-1,3-Oxazoles

Valentin A. Rassadin,* Vadim P. Boyarskiy, and Vadim Yu. Kukushkin*

Institute of Chemistry, Saint Petersburg State University, Universitetskii Pr. 26, Stary Petergof, 198504 Saint Petersburg, Russia

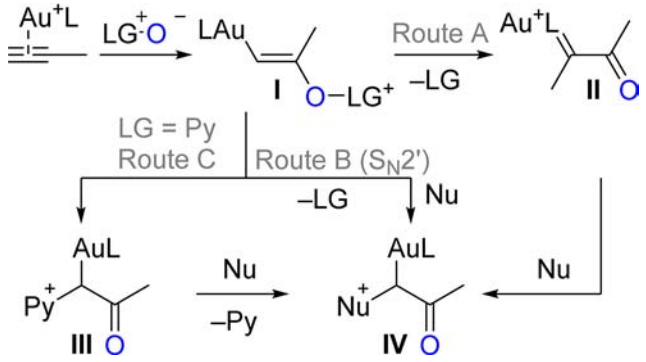
Supporting Information



ABSTRACT: Facile gold-catalyzed heterocyclization based upon intermolecular trapping of the generated α-oxo gold carbenes with various cyanamides R^2R^3NCN (R^2/R^3 = Alk/Alk, $-(CH_2)_2O(CH_2)_2-$, Ar/Ar, Ar/H) has been developed. In most cases, 2-amino-1,3-oxazoles functionalized at the nitrogen atom as well as at the fifth position of the heterocyclic ring (12 examples) were isolated in good to moderate yields.

Homogeneous gold catalysis is among innovative projects of modern organic chemistry.[1] From its many versatile aspects, the one including an oxidation of Au-activated alkyne is particularly important as it provides a facile route to highly reactive electrophilic gold species. The latter can be intra- or intermolecular trapped by various nucleophiles, leading to diverse types of important organic compounds (Scheme 1).[2]

Scheme 1. Generation and Trapping of the Highly Reactive Electrophilic Gold Species



Among many oxidants such as sulfoxides,[3] epoxides,[4] nitrones,[5] or nitro compounds,[6] pyridine *N*-oxides[7] are the most commonly applied to synthetic procedures as these *N*-oxides are efficient in intermolecular oxygen transfer. It is believed that the key intermediates are the highly reactive α-oxo gold carbenes of type **II**, which are formed from initially generated β-gold(I) (vinyloxy)pyridinium species **I** (Scheme 1, route A). However, an alternative pathway, i.e., reaction of **I** with a nucleophile according to the S_N2' type reaction, is also plausible (Scheme 1, route B).[7h] A full account study regarding the role of the α-oxo gold carbenes in the oxidation reactions of alkynes with pyridine oxide employing tandem mass spectrometry, ion spectroscopy, and quantum-chemical calculations has been recently published.[8] It is pointed out that, first, **I** undergoes rearrangement toward more stable intermediate **III**, which serves as a synthetic equivalent of α-oxo gold carbenes (Scheme 1, route C). Second, it is indicated that the existence of naked α-oxo carbenes of type **II** are quite unlikely. Therefore, the reaction might proceed via different routes including several intermediates, and all these routes lead to the same product.

Herein, we report on the trapping of the electrophilic gold species with cyanamides R^2R^3NCN, accomplishing the synthesis of a series of substituted 2-amino-1,3-oxazoles. Heterocycles bearing a 2-amino-1,3-oxazole moiety demonstrate a wide spectrum of biological activity such as antiviral (HIV-1),[9] enzyme (VEGFR2,[10] inosine monophosphate dehydrogenase[11]), and valosin-containing protein[12] inhibition. They behave as TRPV1 receptor antagonist[13] and also as antihelminthic, diuretic, and fungicidal active compounds.[14] Synthetic approaches toward substituted 2-amino-1,3-oxazoles are rather limited.[15,16]

We checked the possibility of formation of the substituted 2-amino-1,3-oxazole with readily available phenyl acetylene (**1a**) and dimethylcyanamide (**2a**) (Table 1). Initial conditions were chosen based on the previous works on gold-catalyzed organic transformations,[7] and the reaction was carried out in neat

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Table 1. Optimization of the Reaction Conditions

	molar ratio of the reagents				
	2a	3	4	5	conditions[a] (yield)
1	5.0	0.05	1.2	2.0	60 °C, 3 h (59%)
2	5.0	0.05		2.0	60 °C, 3 h (7%)
3	5.0	0.05	1.2	2.0	60 °C, 1 h (48%)
4	5.0	0.05	1.2	2.0	60 °C, 2 h (75%)
5	5.0	0.05	1.2	2.0	60 °C, 4 h (61%)
6	5.0	0.05	1.2	2.0	60 °C, 6 h (46%)
7	5.0	0.05	1.2	2.0	23 °C, 3 h (10%)
8	5.0	0.05	1.2	2.0	80 °C, 3 h (64%)
9	5.0	0.10	1.2	2.0	60 °C, 2 h (74%)
10	5.0	0.03	1.2	2.0	60 °C, 2 h (71%)
11	5.0	0.01	1.2	2.0	60 °C, 2 h (26%)
12	3.0	0.03	1.2	2.0	60 °C, PhCl, 2 h (68%)
13	3.0	0.03	1.2	2.0	60 °C, C_6H_6, 2 h (35%)
14	3.0	0.03	1.2	2.0	60 °C, DMF, 2 h (48%)[b]
15	2.0	0.05	1.2	1.0	60 °C, PhCl, 2 h (17%)
16	10	0.05	2.5	4.0	60 °C, PhCl, 2 h (38%)[c]

[a]Isolated yields. [b]2-Oxo-2-phenylethyl formate was isolated as the main product. [c]1,1-Dimethyl-3-(6-methylpyridin-2-yl)urea (7) was isolated in significant amount.

dimethylcyanamide (5.0 equiv) as a solvent by employing 2-picoline oxide as an oxidant. From many suitable gold catalysts, we choose $Ph_3PAuNTf_2$, which is air-stable and can be easily prepared by metathesis reaction from the commercially available Ph_3PAuCl and $AgNTf_2$.[17] In the attempted reaction, target *N*,*N*-dimethyl-5-phenyloxazol-2-amine (**6aa**) was isolated in 59% yield (Table 1, entry 1).

To optimize the reaction conditions, we tested different reagent ratios, amount of the catalyst, solvents, temperature, and reaction time. It is noteworthy that, under the same conditions but in the absence of $MeSO_3H$, oxazole **6aa** was isolated in 7% yield, probably due to deactivation of the catalyst by 2-picoline formed upon the reduction (Table 1, entry 2). On the next step, we modified the reaction time. The best-isolated yield of **6aa** was achieved after 2 h (Table 1, entry 4). Moreover, we noticed that keeping the reaction mixture for more than 2 h at 60 °C (Table 1, entries 5 and 6) did not increase the yield of the target compound and, in addition, resulted in partial decomposition of the product, and all these led to the decreased yield of **6aa**. The effect of temperature was then studied. Reaction was quite slow at rt, and after 3 h oxazole **6aa** was isolated in 10% yield (Table 1, entry 7), although at 80 °C the yield was 64% (Table 1, entry 8). Employing 3 mol % of the catalyst was efficient, whereas when 1 mol % of $Ph_3PAuNTf_2$ was used, the yield of **6aa** decreased dramatically (Table 1, entries 9, 10, and 11, respectively). Therefore, we continued our work employing 3 mol % of the catalyst.

At the initial stage of the project, usage of rather expensive cyanamide **2a** as a solvent was a certain drawback of our approach. To solve this problem, we tested several solvents and tried to reduce amount of the cyanamide. Gratifyingly, chlorobenzene, which was previously employed in a relevant transformations,[7c−e] gave excellent results, viz. 3.0 equiv of the cyanamide and chlorobenzene as a bulk solvent gave the same yield of the target product as for the neat cyanamide (Table 1, entry 12). An unexpected result was obtained when the reaction was carried out in DMF. In this case, 2-oxo-2-phenylethyl formate was isolated (48%) as a major product from the reaction mixture and its appearance is accounted for by the reaction of electrophilic gold species with DMF (Table 1, entry 14). Finally, we tested different amounts of the oxidant and found that when 1.0 equiv of 2-picoline oxide was used, the yield of the target product was 17% (Table 1, entry 15). If a large excess of 2-picoline oxide (4.0 equiv) was employed, a significant amount of 1,1-dimethyl-3-(6-methylpyridin-2-yl)-urea (**7**) was isolated from the reaction mixture (Table 1, entry 16). To summarize optimization of the reaction conditions, we found that performance of the reaction in chlorobenzene with 3.0 equiv of cyanamide **2a**, 2.0 equiv of 2-picoline oxide (**5**), and 3 mol % of $Ph_3PAuNTf_2$ at 60 °C for 2 h leads to the best synthetic results. To verify the scope and limitations of the developed approach, several alkynes and cyanamides were tested (Scheme 2).

First, we tested several cyanamides and observed no or insignificant substitution effect on the reaction time and yield of target 2-amino-1,3-oxazole **6**. All employed cyanamides, viz. dialkylcyanamides, diarylcyanamides, arylcyanamides, and even 4-morpholinecarbonitrile, gave corresponding products in good to moderate yields (78−56%) (Scheme 2).

Second, we demonstrated that terminal aliphatic alkynes as well as phenylacetylene derivatives also yielded **6** in good to moderate yields. We did not observe any significant difference between phenyl acetylenes and its derivatives substituted with strong electron donating (4-$MeOC_6H_4$) or electron withdrawing (2-FC_6H_4) groups. All our experiments indicate that the α-oxo gold carbenoid species can be easily generated, and they are extremely reactive independently on the substitution in the reactants.

When we replaced the terminal alkynes by diphenylacetylene and checked the reactivity of the latter with dimethylcyanamide, we were unable to isolate target *N*,*N*-dimethyl-4,5-diphenyloxazol-2-amine. The conversion of diphenylacetylene was 48% (respective amount of the starting material was recovered from the reaction mixture after column chromatography), and 1,2-diphenylethane-1,2-dione was isolated in 42% yield. However, we detected target *N*,*N*-dimethyl-4,5-diphenyloxazol-2-amine in trace amounts by TLC-HRMS (ESI) technique. The oxidation of diaryl alkynes and ynamides with sulfoxide in the presence of gold(I) salts leading to substituted 1,2-diaryl-1,2-diones was earlier reported.[3e] Later, Hashmi and co-workers extended this approach to a terminal alkyne, however, the reaction was less selective.[7i] Hence, the formation of 1,2-diphenylethane-1,2-dione is not unusual.

To demonstrate the possibility of the scale up synthesis of the target oxazoles, we carried out the reaction starting from 5 mmol of **1a**. In this case, the isolated yield of **6aa** was 76%.

One should mention that a good number of various cyanamides, whose intriguing chemistry is at the early stage of development although they become increasingly popular in recent years,[18] are commercially available. Moreover, disubstituted cyanamides can be easily prepared from amines R^2R^3NH and potassium or sodium cyanate followed by dehydration in the presence of *p*-TsCl in pyridine.[19] Monosubstituted cyanamides are generated from amidoximes

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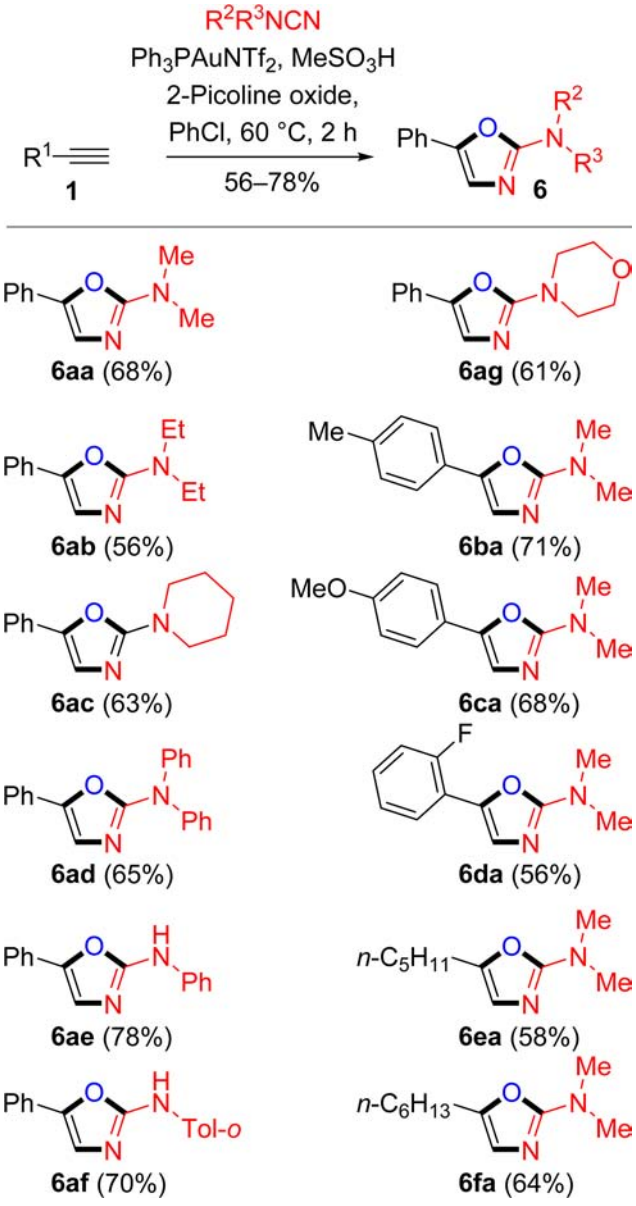
Scheme 2. Reaction Scope with Various Alkynes and Cyanamides

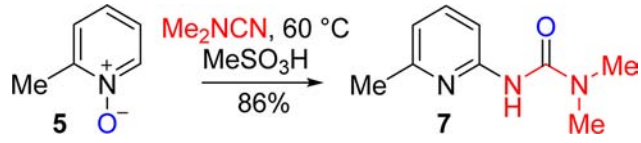


via Tiemann rearrangement in the presence of dehydrating agents like *p*-TsCl in pyridine.[20]

Finally, one should comment on the generation of byproduct **7**. Oxoarylation of nitriles with a pyridine oxide under gold-catalyzed conditions leading to substituted 2-aminopyridines has been recently reported.[7j] However, in our case, the skeleton of the starting alkyne was not incorporated in final product **7**. To understand the role of the gold catalyst and alkyne in this transformation, we modified the reaction conditions and found that the reaction proceeds efficiently only with Me_2NCN taken alone under acid catalysis in the absence of the gold complex, alkyne, or their mixtures. Thus, treatment of a mixture of 2-picoline oxide (**5**) and dimethylcyanamide (**2a**) with methanesulfonic acid at 60 °C gave **7** in 86% yield (Scheme 3).

In our opinion, the observed transformation can be quite useful and we are going to provide a full account research on this reaction in our further works.

Scheme 3. Synthesis of the 1,1-Dimethyl-3-(6-methylpyridin-2-yl)urea (7)



To conclude, we developed a facile gold-catalyzed heterocyclization based on intermolecular trapping of the in situ generated α-oxo gold carbenes with various cyanamides R^2R^3NCN (R^2/R^3 = Alk/Alk, $-(CH_2)_2O(CH_2)_2-$, Ar/Ar, Ar/H) leading to 2-amino-1,3-oxazoles functionalized at the nitrogen atom as well as at the fifth position of the heterocyclic ring. Insofar as the starting materials are easily available, this method can be used for the construction of the chemical libraries containing a wide range of heterocycles bearing an important 2-amino-1,3-oxazole moiety. Further development of the observed gold-catalyzed reaction is underway in our group.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and analytical data of all compounds, copy of the ^1H, $^{13}C\{H\}$, $^{31}P\{H\}$ NMR, and HRMS (ESI) spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01592.

■ AUTHOR INFORMATION

Corresponding Authors

*For V.A.R.: E-mail, v.rassadin@spbu.ru.
*For V.Yu.K.: phone, 78124286890; fax, 78124286939; E-mail: kukushkin@vk2100.spb.edu.

Notes

The authors declare no competing financial interest.

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