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Gold-Catalyzed Hydrohydrazidation of Terminal Alkynes

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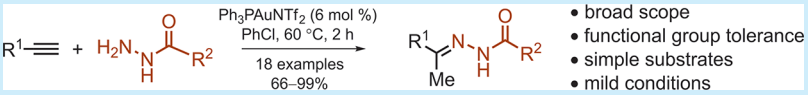
Supporting Information

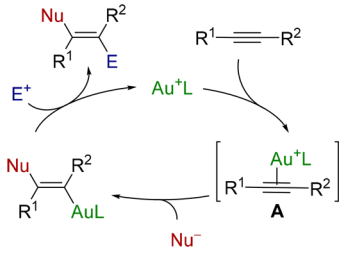


ABSTRACT: Facile gold-catalyzed hydrohydrazidation of alkynes with various hydrazides $R^2CONHNH_2$ (R = Alk or Ar; including those with an additional nucleophilic moiety) in the presence of $Ph_3PAuNTf_2$ (6 mol %) leading to a wide range of substituted keto-*N*-acylhydrazones (18 examples) in excellent to good yields (99−66%) is reported. This novel metal-catalyzed coupling proceeds under mild conditions (chlorobenzene, 60 °C), exhibits high functional group tolerance, and is insensitive to the electronic and steric effects of the substituents in the reactants.

Gold-catalyzed organic transformations stand among the cutting-edge topics[1,2,11,3−10] of modern chemistry, and in particular, these reactions are widely employed in the key steps of total synthesis of natural products.[12,13] Gold-based catalysis is also used for the synthesis of varieties of heterocyclic systems, which find numerous applications in medicinal chemistry.[14−25] The success of Au-catalyzed reactions is typically based on high functional group tolerance and mild reaction conditions.

Most common applications of the gold-involving catalysis incorporate activation of unreactive alkynes toward nucleophilic addition (Scheme 1). It is generally believed that the

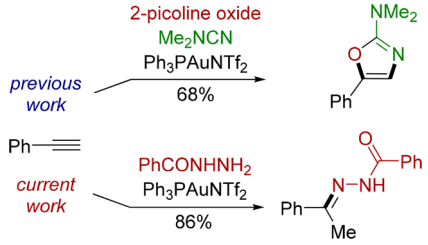
Scheme 1. Generation and Trapping of the Highly Reactive Electrophilic Au^I Species



reaction of alkynes proceeds through an Au-activated alkyne complex[9] **A** before it is attacked by nucleophiles such as water,[26−28] alcohols,[29−31] primary[32−35] or secondary amines,[36,37] or hydrazines.[38−40] The Au^I-catalyzed reaction with hydrazides relevant to this work has never been studied in the past.

Previously, we have demonstrated that the multicomponent reaction between alkynes, cyanamides, and pyridine *N*-oxides in the presence of 5 mol % of $Ph_3PAuNTf_2$ is a synthetically significant approach for the preparation of a series of substituted 2-amino-1,3-oxazoles (Scheme 2).[41] In an attempt to expand the scope of the developed transformation, we have surprisingly found that a simple replacement of cyanamide with benzohydrazide dramatically changed the result. Thus,

Scheme 2. Different Routes of the Au-Catalyzed Reactions of Alkynes



benzohydrazide reacted smoothly with phenylacetylene in the presence of $Ph_3PAuNTf_2$ to yield the appropriate acylhydrazone, whereas pyridine *N*-oxides did not participate in the observed transformation.

To the best of our knowledge, such gold-catalyzed coupling of *N*-nucleophiles and alkynes is hitherto unknown, and there have been no reports concerning even similar reactions of hydrazides. Only for the synthesis of gold−carbene complexes have *N*-acylhydrazines been used.[42] Our interest in the gold(I)-catalyzed hydrohydrazination was further stimulated by the available evidence that keto-*N*-acylhydrazones, formed in the reaction, demonstrate antiviral (influenza A,[43] HSV-1[44]), antitubercular,[45,46] antiproliferative,[47] anticonvulsant,[48,49] and antimicrobial[50] activities, act as LSD-1[51] and G3BP2[52] inhibitors, and additionally are broadly employed in organic synthesis.[53−57] Herein, we report on a new high-yielding approach toward acylhydrazones, which are generated under mild conditions through nucleophilic addition of hydrazides to alkynes in the presence of gold(I).

Initially, this reaction was carried out in chloroform at 60 °C employing 6 mol % of $Ph_3PAuNTf_2$ and an equimolar ratio of phenylacetylene (**1a**) and benzohydrazide (**2a**). In the attempted reaction, the target benzoylhydrazone (**4aa**) was isolated in a moderate yield (66%; Table 1, entry 1). In order

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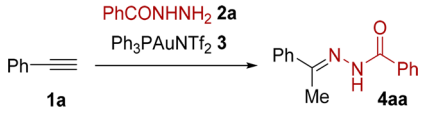
to optimize the reaction conditions, we tested various solvents, temperature, reagent ratios, amount of the catalyst, and reaction time (Table 1).

Table 1. Optimization of the Hydrohydrazidation Conditions



	conditions[a]			
	solvent	temp (°C)	time (h)	yield[b] (%)
1	$CHCl_3$	60	1	66
2	MeCN	60	1	66
3	DMF	60	1	traces[c]
4	EtOH	60	1	68
5	PhCl	60	1	81
6	PhCl	90	1	83
7	PhCl	110	1	59
8	PhCl	60	2	92
9	PhCl	60	3	90
10	PhCl	60	2	91[d]
11	PhCl	60	2	83[e]

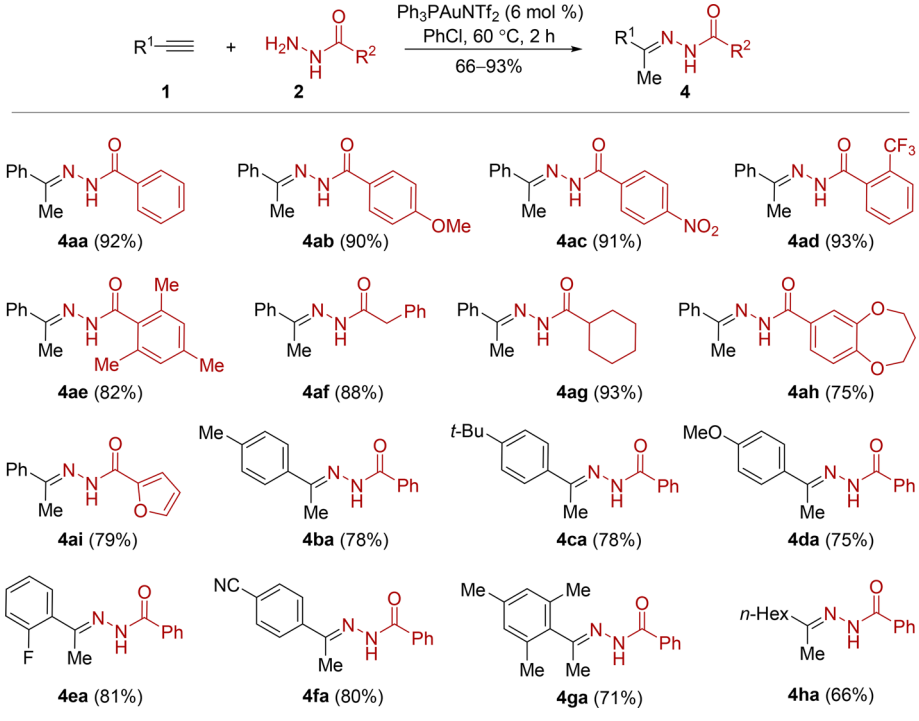
[a]An equimolar ratio of **1a**/**2a** was used. [b]Isolated yield. [c]Traces of the product were detected in reaction mixture using ESI-MS. [d]1.2 equiv of **1a** was used. [e]3 mol % of $Ph_3PAuNTf_2$ was used.

First, we varied a few common solvents of different natures (MeCN, DMF, EtOH, PhCl) and found that the application of chlorobenzene led to the best synthetic results (Table 1, entries 1−5). The effect of temperature and reaction time was then studied. Increasing the temperature by 30 °C did not significantly change the yield of benzoylhydrazone **4aa** (Table 1, entry 6), whereas the isolated yield of **4aa** dropped off to 59% when the reaction was conducted at 110 °C. The decrease of the yield is probably because of a partial decomposition and/or instability of the catalyst at 110 °C (Table 1, entry 7). Regarding the reaction time, we observed that keeping the reaction mixture at 60 °C for 2 h brings about an increase of the isolated yield of **4aa** up to 92% (Table 1, entry 8). Longer heating as well as usage of a small excess of phenylacetylene did not improve the yield (Table 1, entries 9 and 10). Finally, we found that with a lower amount of $Ph_3PAuNTf_2$ (3 mol %) the target hydrazone was isolated in 83% yield (Table 1, entry 11).

To verify the scope and limitations of the developed approach, several alkynes and hydrazides were tested (Scheme 3). In most cases, hydrazides **2** were obtained from easily available carboxylic acid esters and hydrazine hydrate and isolated in excellent yields. Commercially unavailable alkynes **1** were synthesized either from aryl halides through Sonogashira coupling[58] or from the appropriate aldehyde employing Bestmann−Ohira reagent[59] (for more details, see the Supporting Information).

First, we tested several substituted benzohydrazides **1** bearing strong electron-donating (4-$MeOC_6H_4$) or strong electron-withdrawing (4-$NO_2C_6H_4$, 2-$F_3CC_6H_4$) groups and observed no or very small substitution effect on the reaction time and yield of target *N*-acylhydrazones **4**. Surprisingly sterically hindered 2,4,6-trimethylbenzohydrazide (**2e**) reacted smoothly with phenylacetylene (**1a**), and in this particular case, the target product was isolated in good yield (82%). Hydrazides obtained from aliphatic carboxylic acids such as phenylacetic acid and cyclohexanecarboxylic acid gave target products **4af** and **4ag** in 88 and 93% yields, respectively. To demonstrate the potency of the developed approach, we prepared heterocyclic hydrazides, viz. 3,4-dihydro-2*H*-benzo-[*b*][1,4]dioxepine-7-carbohydrazide (**2h**) and furan-2-carbohydrazide (**2i**) and employed these species in the studied

Scheme 3. Reaction Scope with Various Terminal Alkynes and Hydrazides



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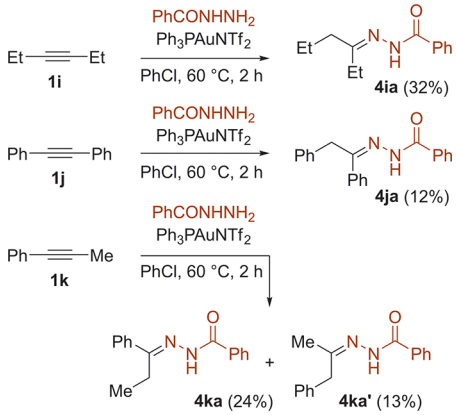
system. These attempts were successful, and in both cases, the corresponding products were isolated in 75 and 93% yields.

Second, we checked the behavior of terminal and internal alkynes. In general, terminal alkynes were more reactive, and the desired hydrazones **4** were formed in better yields than in the case of internal triple bond species. Thus, derivatives of the phenylacetylene bearing moderate electron-donating (4-MeC_6H_4, 4-*t*-BuC_6H_4), strong electron-donating (4-$MeOC_6H_4$), and electron-withdrawing groups (2-FC_6H_4, 4-NCC_6H_4) as well as alkynes featuring bulky substituents next to the reaction center (2,4,6-$Me_3C_6H_2$) reacted smoothly, and in all cases, acylhydrazones **4ba**–**ga** were isolated in good yields (71–81%). Expectedly, oct-1-yne reacted in the same way as phenylacetylene. *N*′-(Octan-2-ylidene)benzohydrazide (**4ha**) was obtained in 66% yield. All of our experiments indicate that the Au-activated species[9] can be easily generated from terminal alkynes, and they exhibit high reactivity independent of the substitution in the reactants.

When terminal alkynes were replaced by internal species **1i**–**k**, we observed a significant decrease of the reactivity and **4ia**–**ka** species were obtained in extremely low yields. However, application of 12 mol % of $Ph_3PAuNTf_2$ allowed a slight improvement of the yield of **4** (Scheme 4) Thus, for hex-3-yne,

Scheme 4. Reaction of Internal Alkynes with Benzohydrazide (2a)

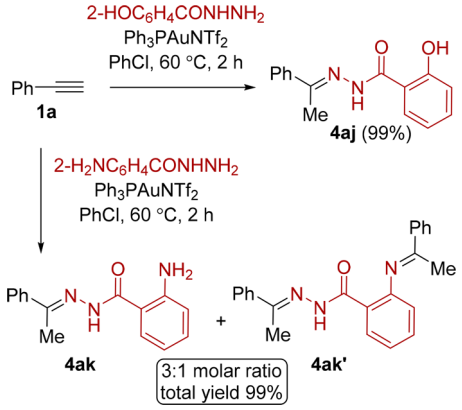


the corresponding *N*′-(hexan-3-ylidene)benzohydrazide (**4ia**) was isolated in moderate yield (32%), whereas sterically hindered 1,2-diphenylacetylene was unreactive, and target *N*′-(1,2-diphenylethylidene)benzohydrazide (**4ja**) was isolated in only intermediate yield and its application in the system gave a mixture of regioisomers (a molar ratio 2:1) in total 37% yield. All of these results indicate that the developed approach could not be recommended as a synthetic procedure for the preparation of acylhydrazones **4** from internal alkynes. In our opinion, the problem of the low reactivity of internal alkynes could be solved by using a more catalytically active gold species, and this work is under way in our group.

The coupling proceeds unconventionally when benzohydrazides **2j**–**l** bearing an additional nucleophilic moiety were applied as the reaction partners (Scheme 5). Thus, 2-hydroxybenzohydrazide (**2j**) reacted selectively, and we observed only coupling of the alkyne and the $NHNH_2$ functional group. The 2-hydroxy-*N*′-(1-phenylethylidene)-benzohydrazide (**4aj**) was isolated in 99% yield.

In the case of 2-aminobenzohydrazide (**2k**), the amino group also took part in the transformation, and two products

Scheme 5. Reaction of Phenylacetylene (1a) with Bidentate Nucleophiles 4j–k



(a molar ratio ca. 3:1) were formed in 99% overall yield. The desired acylhydrazone **4ak** was isolated as the major product (58%), whereas the byproduct was formed after addition of the second molecule of phenylacetylene (**1a**). For 2-mercaptobenzohydrazide (**2l**), only traces of 2-mercapto-*N*′-(1-phenylethylidene)benzohydrazide (**4al**) were detected in the reaction mixture by HRESI-MS, most likely as a result of possible deactivation of the gold(I) species by sulfur-containing hydrazide under the reaction conditions; the high affinity of gold(I) toward sulfur is well-known.

In the context of the hydrohydrazidation, we were interested in comparison of the reactivities of hydrazides and hydrazines. Although these two classes of compounds are structurally relevant, their reactivity in the studied transformation is not the same. We found that the $Ph_3PAuNTf_2$-catalyzed coupling of $PhC(=O)NHNH_2$ with PhCCH proceeds differently than the attempted reaction with $PhCH_2NHNH_2$. It appears that the hydrazine $PhCH_2NHNH_2$ does not react with phenylacetylene under the optimized conditions because it reduces the $Ph_3PAuNTf_2$ catalyst to colloid gold (detected after the treatment).[40,60–62] Furthermore, the reaction between PhCCH (**1a**) and benzohydrazide (**2a**) is totally suppressed when the equimolar amount of benzylhydrazine is added to the reaction mixture, again because of the poisoning of the catalyst by its reduction.

The contrasting reactivity of the hydrazides and hydrazines could be rationalized upon consideration of the literature data. Thus, a kinetic study indicated that $RC(=O)NHNH_2$ are 30–70 times less nucleophilic than $RNHNH_2$,[63] and in addition, more electron-deficient $RC(=O)NHNH_2$ species are weaker reducing agents than the relevant hydrazines.[64] Most likely, the electron-accepting RC(=O) group reduces nucleophilicity of hydrazides and, concurrently, makes them substantially weaker reducing agents than the relevant hydrazines, thus determining the success of the studied gold-catalyzed reaction.

To conclude, we developed a facile gold-catalyzed hydrohydrazidation based on an intermolecular reaction of the in situ generated Au-activated terminal alkynes[9] with various hydrazides $R^2CONHNH_2$ (R^2 = Alk or Ar) leading to keto-*N*-acylhydrazones. In the case of phenylacetylene derivatives or substituted benzohydrazides, the developed reaction proceeds under mild conditions, exhibits high functional group tolerance, and is insensitive to the electronic and steric effects of the substituents in the aromatic ring, and in all studied

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instances, the target acylhydrazones were isolated in excellent to good yields.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02019.

Experimental procedures and analytical data of all compounds; ^{1}H, $^{13}C\{H\}$ and HRMS (ESI) spectra (PDF)

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Notes

The authors declare no competing financial interest.

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