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Cu(I)-Catalyzed Oxidative Cyclization of Alkynyl Oxiranes and Oxetanes

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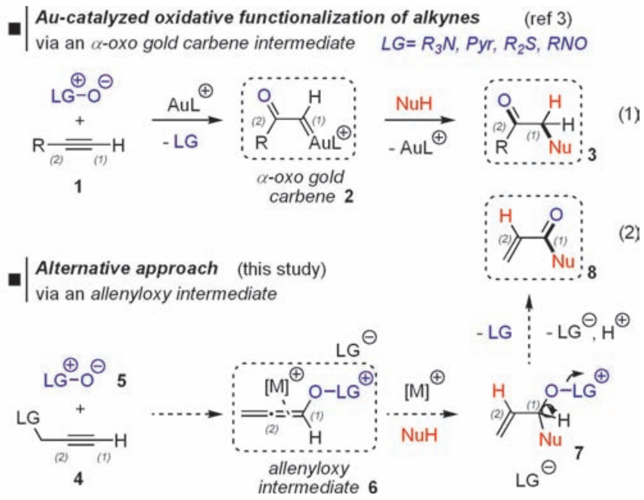
Supporting Information

ABSTRACT: In the presence of a Cu(I) catalyst and a pyridine oxide, alkynyl oxiranes and oxetanes can be converted into functionalized five- or six-membered *α,β*-unsaturated lactones or dihydrofuranaldehydes. This new oxidative cyclization is proposed to proceed via an unusual allenyloxypyridinium intermediate.

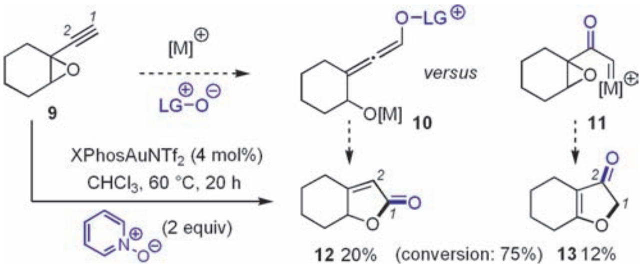
Among the variety of gold-catalyzed transformations that have been developed to date,[1] those concerning the *oxo functionalization of alkynes* have attracted special interest.[2] They indeed allow an unconventional and efficient access to a range of molecules that cannot be easily synthesized using other methods. These transformations, which take advantage of the *π*-acid/electron-donor dual reactivity of gold species, involve the formation of an *α*-oxo gold carbene intermediate that is generated after an initial intra- or intermolecular nucleophilic addition of an oxygen donor (amine oxide, sulfoxide, nitro, etc.) onto a gold-activated alkyne.[3] In the case of a terminal alkyne **1**, this process leads to the *regioselective* formation of a gold carbene **2**, which can then be trapped by a nucleophile to furnish the functionalized keto derivative **3** (eq 1).



Following our continuous interest in metal-mediated transformations of alkynes,[4] we were intrigued by the possibility of developing an *alternative oxidative functionalization of alkynes* based on the use of terminal alkynes of type **4** (eq 2). We conceived that the presence of a leaving group (LG) in **4** might be used to generate an unusual allenyloxy intermediate **6** by an S_N2'-type addition of an oxidizing agent **5** at the terminal position of the alkyne. Subsequent activation of **6** by an electrophilic metal could potentially induce the addition of a nucleophile at carbon C(1) of the allene moiety and ultimately lead to the formation of *α,β*-unsaturated keto compound **8** via **7**. In contrast to what was previously reported (eq 1), this approach would allow the introduction of both the oxygen atom and the nucleophile at the same terminal position of the alkyne (eq 2).

Alkynyl oxiranes such as **9**, which are prone to undergo metal-mediated S_N2'-type additions,[5] were first chosen as model substrates to study the feasibility of this general approach (Scheme 1). In this case, the addition of an oxidizing agent at the terminal position of the alkyne could produce a metal alkoxide such as **10** that would play the role of the functionalizing nucleophile in our scenario (LG = Nu in eq 2).

Scheme 1. First Attempt at Oxidative Cyclization with Alkynyl Oxirane Model Substrate 9 (LG = Nu in eq 2)



On the basis of recent work concerning the oxidative functionalization of alkynes using gold(I) complexes and pyridine oxides[3d−i] and the already reported possibility of activating alkynyl oxiranes with gold species,[6] substrate **9** was treated with 4 mol % $XPhosAuNTf_2$[7] and 2 equiv of pyridine oxide in refluxing chloroform (Scheme 1). The reaction was slow and led to the formation of multiple products, among which the two isomeric oxidized products **12** and **13**, which differ by the presence of a carbonyl functionality at either C(1) or C(2), could be identified.

Although this transformation was inefficient and unselective, the formation of the unsaturated lactone **12** validated our approach (eq 2), since both the oxygen atom and the functionalizing

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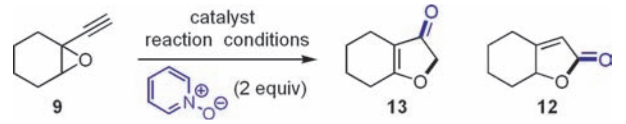
nucleophile were introduced at the terminal position of the alkyne in this case. The competitive formation of the isomeric furan-3-one **13** could be explained by nucleophilic trapping of the alternative α-oxo gold carbene intermediate **11** by the epoxide moiety following a process similar to that presented in eq 1.

We next screened various experimental conditions to optimize the formation of **12**. The main results of this study are compiled in Table 1. Changing the nature of the gold catalyst did not markedly improve the efficiency of the reaction (entries 1−3), and a maximum 38% yield of **12** was obtained when IPrAuNTf$_2$[8] was used as the catalyst (entry 3).[9] Interestingly, silver salts showed higher reactivity (entries 4−6), and an improved 65% yield of **12** was obtained when **9** was reacted with 10 mol % AgOTf in refluxing acetonitrile for 20 h (entry 6). Notably, no trace of furan-3-one **13** was observed under these conditions, thus highlighting the striking difference in reactivity between gold and silver catalysts. We next attempted the reaction with softer Lewis acidic copper(I) catalysts (entries 7−10). We were delighted to observe that **12** could be selectively obtained in an excellent yield of 92% when AgOTf was replaced by the Cu(NCMe)$_4$OTf complex (10 mol %) (entry 7). An additional screening of various counteranions showed that the rate of the reaction could be noticeably enhanced when the complex Cu(NCMe)$_4$NTf$_2$ (**14**) was used as the catalyst (entry 9).[10,11] The catalyst loading could even be reduced, and the desired lactone **12** was finally obtained in 98% yield when **9** was treated with 4 mol % **14** in refluxing acetonitrile for 8 h (entry 10). Furthermore, copper(II) catalysts were less reactive,[12] and no trace of **12** was observed with HNTf$_2$[13] or in the absence of a catalyst (entries 11−13).[14]

Table 1. Optimization of the Catalytic System[a]

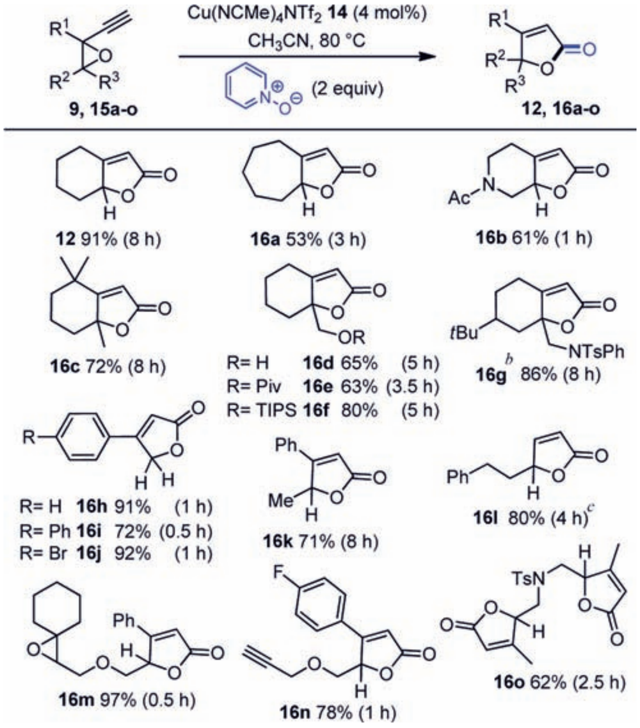


entry	catalyst		conditions	conversion[b]	yields[b] 13	yields[b] 12
1	XPhosAuNTf$_2$	4 mol%	CHCl$_3$, 60 °C, 20 h	75%	12%	20%
2	IPrAuNTf$_2$	4 mol%	CHCl$_3$, 60 °C, 20 h	100%	5%	38%
3	AuCl$_3$	4 mol%	CHCl$_3$, 60 °C, 20 h	100%	18%	0%
4	AgNTf$_2$	10 mol%	CHCl$_3$, 60 °C, 20 h	78%	0%	51%
5	AgOTf	10 mol%	CHCl$_3$, 60 °C, 20 h	90%	0%	49%
6	AgOTf	10 mol%	CH$_3$CN, 80 °C, 20 h	100%	0%	65%
7	Cu(NCMe)$_4$OTf	10 mol%	CH$_3$CN, 80 °C, 20 h	100%	0%	92%
8	Cu(NCMe)$_4$PF$_6$	10 mol%	CH$_3$CN, 80 °C, 0.5 h	100%	0%	63%
9	Cu(NCMe)$_4$NTf$_2$	10 mol%	CH$_3$CN, 80 °C, 2.5 h	100%	0%	96%
10	Cu(NCMe)$_4$NTf$_2$ **14**	4 mol%	CH$_3$CN, 80 °C, 8 h	100%	0%	98%[c]
11	CuCl$_2$ AgNTf$_2$	10 mol% 20 mol%	CH$_3$CN, 80 °C, 24 h	100%	0%	74%
12	HNTf$_2$	4 mol%	CH$_3$CN, 80 °C, 20 h	100%	0%	0%
13	—		CH$_3$CN, 80 °C, 20 h	0%	0%	0%

[a] **9**: 0.1 mmol. [b] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] 91% isolated yield (**9**: 2 mmol).

Having in hand optimal reaction conditions for the oxidative cyclization of **9** (Table 1, entry 10), we explored the scope of this new transformation. As shown by the results compiled in Scheme 2, a wide range of alkynyl oxiranes **15a−o** could be converted into the corresponding lactones **16a−o** in yields of 53−97%. The reaction could be performed with cyclic (**12**, **16a−g**) as well as acyclic (**16h−o**) alkynyl oxiranes possessing a range of common functional groups, including an ester (**16e**), an amide (**16b**, **16g**, and **16o**), an alkyl or silyl ether (**16f**, **16m**, and **16n**), an alcohol (**16d**), or a halogen (**16j** and **16n**). No variation in efficiency was observed when the degree of substitution of the epoxide was varied (from di- to tetrasubstituted epoxides), whereas a *cis*-epoxide was found to react as rapidly as its trans isomer (**16l**).[15] Notably, the transformation was selective toward the conversion of the alkynyl oxirane moiety, since simple terminal alkyne or epoxide functionalities remained untouched during the process (**16m** and **16n**). The transformation was also successfully applied to the synthesis of the natural product (±)-dihydroactinidiolide (**16c**).[16,17]

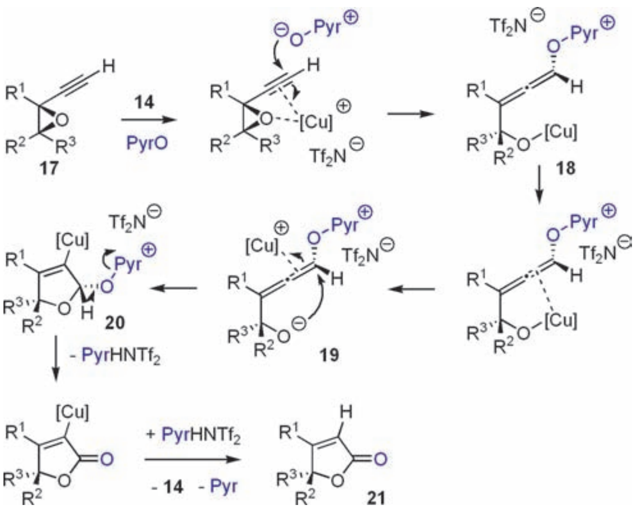
Scheme 2. Reaction Scope: Alkynyl Oxiranes



[a] Isolated yields. [b] d.r. of starting material = 1:1.25. [c] cis:trans ratio of starting material = 1:1.3.

A mechanistic proposal for the oxidative cyclization of alkynyl oxiranes is presented in Scheme 3. Potential dual coordination

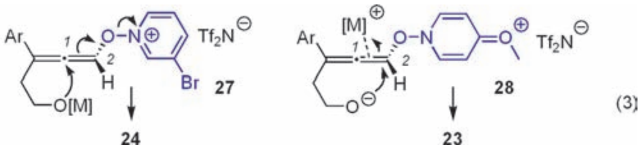
Scheme 3. Mechanistic Proposal



of the copper(I) complex to both the alkyne and epoxide moieties in **17**[18] could induce nucleophilic addition of the pyridine oxide at the terminal position of the alkyne and the consequent formation of the allenyloxypyridinium intermediate **18**. Subsequent intramolecular activation of the allene moiety by the copper alkoxide[19] could lead to the formation of the cyclic vinylcopper intermediate **20**, possibly via **19**. A final proton loss[20]/protodemetalation sequence would deliver the cyclic lactone **21** with concomitant regeneration of the catalyst.[21,22]

To highlight further the synthetic potential of this new oxidative cyclization, we envisaged its application to the conversion of homologous alkynyl oxetanes. This would lead to the formation of the important six-membered unsaturated lactone structural unit, which is frequently found in natural products. Oxetane **22** was therefore submitted to the optimized reaction conditions used for the oxidative cyclization of alkynyl oxiranes (Table 2, entry 1).

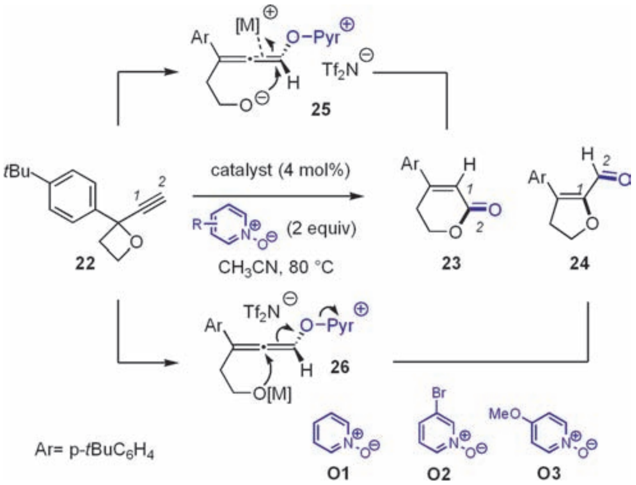
The oxidative process was rapid and efficient but surprisingly delivered a 1:1.9 mixture of the desired lactone **23** and the unexpected dihydrofuranaldehyde **24**.[23] We attempted to optimize the formation of both **23** and **24**, conceiving that these compounds could originate from the same allenyloxypyridinium intermediate. Lactone **23** could indeed be formed by a 6-endo cyclization via **25**, analogously to the case of alkynyl oxiranes, while the dihydrofuranaldehyde **24** might be produced by a competitive 5-exo cyclization via **26**. We first changed the catalyst, hoping that the use of a more Lewis acidic species would favor the formation of **23** by stronger coordination of the metal to the allene moiety in **25**. To this end, alkynyl oxetane **22** was treated with $AgNTf_2$ and pyridine oxide in refluxing acetonitrile (Table 2, entry 2). Unfortunately, even though an increased quantity of lactone **23** was formed (**23**:**24** = 1.1:1), the reaction remained unselective. We next envisaged modifying the oxidant. The use of a more electron-deficient pyridine oxide, such as 3-bromopyridine oxide (**O2**), could favor the formation of **24** since the corresponding 3-bromopyridine group in **27** would act as a better leaving group during the 5-exo cyclization step (eq 3). Conversely, the use of a more electron-rich pyridine oxide, such as 4-methoxypyridine oxide (**O3**), should favor the formation of **23** because the positive charge in **28** would be partially delocalized far from the reacting allene center (eq 3). Gratifyingly, treatment of **22** with 4 mol % $Cu(NCMe)_4NTf_2$ in the presence of either **O2** or **O3** led to the efficient and completely selective formation of **24** (85%) or **23** (74%), respectively (Table 2, entries 3 and 4).[24] These two sets of experimental conditions were then applied to a series of alkynyl oxetanes in order to delineate the scope of the transformation. As shown in Scheme 4, a range of diversely substituted alkynyl oxetanes **29a−f** could be selectively converted into the corresponding dihydrofuranaldehydes **30a−d** (72−88%) or lactones **31a−f** (67−89%) simply by varying the nature of the pyridine oxide.[25,26]



(3)

In summary, we have developed a new and efficient oxidative cyclization of alkynyl oxiranes or oxetanes into the corresponding α,β-unsaturated lactones. This copper(I)-catalyzed transformation, which presumably proceeds via the formation of an unusual allenyloxypyridinium intermediate, takes place under mild conditions using a simple pyridine oxide as the oxidant and is compatible with a wide range of common functional groups. Additionally, an interesting divergence in product selectivity was uncovered in the case of alkynyl oxetanes, as these can be converted into either lactones or dihydrofuranaldehydes depending on the nature of the pyridine oxide employed.

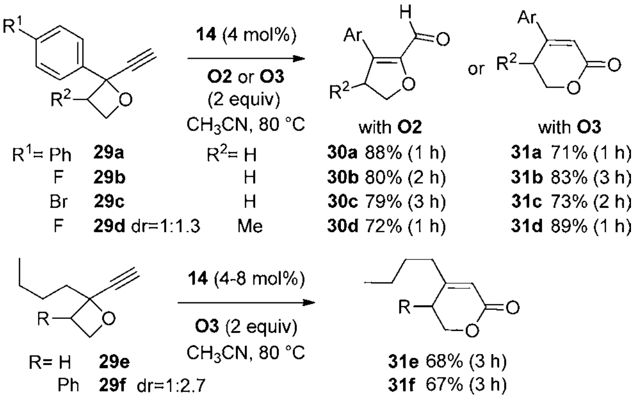
Table 2. Oxidative Cyclization of Alkynyl Oxetane 22[a]



entry	catalyst	oxide	time	23:24 ratio[a]	yield[b] (23+24)
1	$Cu(NCCH_3)_4NTf_2$ **14**	**O1**	1.5 h	1 : 1.9	84%
2	$AgNTf_2$	**O1**	2.25 h	1.1 : 1	81%
3	$Cu(NCCH_3)_4NTf_2$ **14**	**O2**	1 h	0 : 1	85%[c]
4	$Cu(NCCH_3)_4NTf_2$ **14**	**O3**	3 h	1 : 0	74%[c]

[a]Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [b]Determined by ^{1}H NMR spectroscopy of the crude reaction mixture using 1,2-dichloroethane as an internal standard. [c]Isolated yield.

Scheme 4. Oxidative Cyclization of Alkynyl Oxetanes



■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) A furan was also obtained with these Au catalysts (15–70%) (see ref 6).

(10) **14** was easily synthesized from Cu_2O and $NHTf_2$(aq) in CH_3CN by adapting the procedure described in: Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90 (see the SI for more details). For a seminal use of **14** in cycloisomerization reactions, see: Fehr, C.; Vuagnoux, M.; Buzas, A.; Arpagaus, J.; Sommer, H. *Chem.—Eur. J.* **2011**, *17*, 6214.

(11) Only degradation was observed when acetonitrile was replaced with chloroform.

(12) Other copper(II) or iron(III) catalysts (10 mol %) gave lower yields and longer reaction times: [$CuCl_2$] 4 h, 37%; [$CuCl_2$, $2AgBF_4$] 18 h, 78%; [$CuCl_2$, 2AgOTf] 24 h, 71%; [Cu_2O] 24 h, 0%; [$FeCl_3$, 3AgOTf] 24 h, 17%.

(13) Only degradation was observed.

(14) Other pyridine oxides such as 4-phenyl- or 4-methoxypyridine oxide gave lower yields and longer reaction times. No reaction took place when dimethyl sulfoxide was used as the solvent or diphenyl sulfoxide (2 equiv) as the oxidizing agent.

(15) Monitoring the reaction of **15l** by ^1H NMR spectroscopy showed that the cis and trans isomers were consumed at the same rate. A difference was observed for the 1:1.25 diastereoisomeric mixture **15g**: one of the diastereoisomers was completely consumed in 4 h, while 8 h was required for the second one.

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(17) No reaction or degradation occurred with internal alkynes.

(18) Dual coordination of the catalyst was previously proposed for Au- and Ag-catalyzed transformations of alkynyl oxiranes (see ref 6).

(19) No intermediate, and especially no allenic alcohol corresponding to the protonated form of **19**, was observed when the reaction was monitored by ^1H NMR spectroscopy. An allene-coordinated copper(I) alkoxide has been recently proposed as an intermediate in another Cu(I)-catalyzed transformation. See: Sai, M.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3294.

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(21) The exact nature of the Cu(I) active species is not known, as the pyridine oxide and the pyridine generated during the process could bind to the metal center.

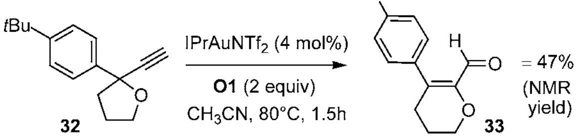
(22) A mechanism involving the formation of an allenylidene copper(I) species via a copper(I) acetylide could be envisaged (see: Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; van Maarseveen, J. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3777). However, while such a mechanism cannot be ruled out, it is not supported by an experiment performed in the presence DIPEA [an additional base that should favor the formation of a copper(I) acetylide]. In this case, the rate of the reaction was indeed extremely reduced. Moreover, this mechanism does not easily explain the competitive formation of dihydrofuranaldehydes when alkynyl oxetanes are used as substrates.

(23) Compound **24** could not be converted into **23** under the reaction conditions employed.

(24) Very similar results were obtained with $AgNTf_2$.

(25) Surprisingly, the corresponding dihydrofuranaldehydes could not be obtained when **29e** and **29f** were used as substrates.

(26) $Cu(NCMe)_4NTf_2$ was not able to catalyze the reaction of alkynyl tetrahydrofuran **32**. However, when $IPrAuNTf_2$ was used, the corresponding aldehyde was obtained in moderate yield.



(4)