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# Gold-Catalyzed Highly Efficient Access to 3(*2H*)-Furanones from 2-Oxo-3-butynoates and Related Compounds

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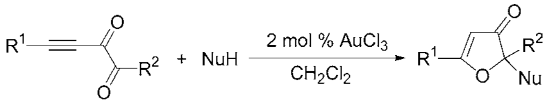
## ABSTRACT



$R^1$= aryl, alkyl, alkenyl; $R^2$= alkoxy, alkyl, alkynyl

**The gold-catalyzed cyclization reactions of 2-oxo-3-butynoic esters or disubstituted-1,2-diones with a variety of nucleophiles are described, which offer an efficient and straightforward route to substituted 3(*2H*)-furanones under mild reaction conditions. The Au(III) catalysts are also highly effective in the hydration of these activated alkynes.**

The 3(*2H*)-furanones constitute an important class of heterocyclic compounds that are of pharmacological significance and represent useful building blocks for natural products syntheses.[1] A large number of naturally occurring antibiotics, antitumors, and antiinsectans such as jatrophone,[1a,b] geiparvarin,[1c,d] eremantholides,[1e] trachyspic acid,[1f] lychnophorolide A,[1g] ciliarin,[1h] 2-deoxysiphonarien furanone,[1i] and the recently reported metabolite longianone[1j,k] possess the 3(*2H*)-furanone ring as a central structural element. Substituted 3(*2H*)-furanones have been prepared mainly by acid-induced cyclization−dehydration of α′-hydroxy-1,3-diketones,[2] cyclization of dianion equivalents with α-chloroacetic acid chlorides,[3] aldol reaction of 3-silyloxyfurans with aldehydes in the presence of a Lewis acid,[4] transformation of 3-alkoxyfurans to 2-alkoxy-3-furanones with PTAB,[5] or hydrogenolysis and acidic hydrolysis of isoxazoles.[6] The synthetic methods developed so far, however, have some drawbacks

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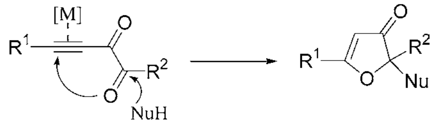
such as lack of satisfactory general preparative procedures for starting substrates.[6] As a result of the increased interest in this important heterocycles, methods are needed to enhance the efficiency of the synthesis of these compounds and generate the 3(*2H*)-furanones with a wide variety of substituents. On the other hand, transition-metal-catalyzed heteroannulation reactions have been developed with remarkable improvements in terms of efficiency and wide scope of application;[7] however, there is no report for the construction of 3(*2H*)-furanones using transition metal methods. It has recently been shown that Au(III) salts and Au(I) complex display considerable catalytic activity under moderate conditions.[8] The activation of alkynes or allenes with carbophilic, Lewis-acidic gold salts is the most widespread application of homogeneous gold catalysis, and it is also utilized for the construction of carbocyclic or heterocyclic compounds.[9] We are particularly interested in the transition-metal-catalyzed cyclization of allenyl ketones[10] and 3-alkyn-1-ones.[11] It has been reported that gold catalysts are highly efficient for this type of reaction as a result of the excellent alkynophilicity of gold.[12] For example, Larock et al. reported an interesting $AuCl_3$-catalyzed cyclization of 2-(1-alkynyl)-2-alken-1-ones leading to substituted furans.[13] In our ongoing efforts to develop new methodologies for the synthesis of heterocycles promoted by gold,[14] we envisioned that the activated alkynes such as 2-oxo-3-butynoic esters or related compounds might also undergo metal-catalyzed cyclization to substituted 3(*2H*)-furanones (Scheme 1). Herein, we report the utilization of gold as catalyst for cyclization of activated alkynes, which offers a convenient and general approach to 2,2-disubstituted-3(*2H*)-furanones under extremely mild reaction conditions. The gold-catalyzed hydration of these alkynes in yields up to 88% with high stereoselectivity is also presented.

**Scheme 1.** Strategy for Metal-Catalyzed Formation of 3(*2H*)-Furanones



The requisite 2-oxo-3-butynoates and dialkynyl-1,2-diones were easily synthesized by copper-catalyzed cross-coupling reaction of terminal alkynes and monooxalyl chloride or oxalyl chloride in good to high yields.[15] 1-Phenyl-1-pentyne-3,4-dione **1e** was prepared from 1-(benzotriazol-1-yl)propargyl ethyl ethers.[16] We began our investigation with 2-oxo-4-phenylbut-3-ynoic acid isopropyl ester **1a** ($R^1$ = Ph, $R^2$ = $O^i$Pr) bearing a phenyl group (Table 1). To our delight, the concept works nicely. Treatment of **1a** with 2 mol % $AuCl_3$ (used as a 0.05 M solution in $CH_3CN$) and 1.5 equiv of methanol in $CH_2Cl_2$ afforded the corresponding 2,2-dialkoxy-3(2*H*)furanone **2a** smoothly in 81% yield after stirring at room temperature for 3 h. No other additive was needed for this reaction. In the absence of $AuCl_3$ catalyst, no reaction took place. This result indicates that $AuCl_3$ is required for the reaction to proceed. The cationic gold(I) complex $(PPh_3)$-AuCl/AgOTf also showed good catalytic activity in $CH_2Cl_2$ to afford 75% of **2a** (84% in THF).

The yield was decreased to 69% when using 0.1% of $AuCl_3$. To rule out a possible involvement of Brønsted acid catalysis, the reaction mixture of **1a** with MeOH was treated with 10% of HCl in the absence of $AuCl_3$. Only a trace

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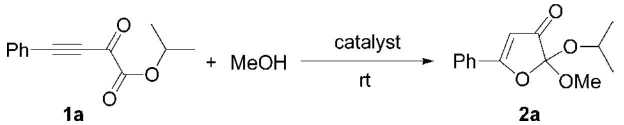
(16) Katritzky, A. R.; Lang, H. *J. Org. Chem.* **1995**, *60*, 7612.

**Table 1.** Gold-Catalyzed Cyclization of 2-Oxo-3-butynoate **1a**



**1a** **2a**

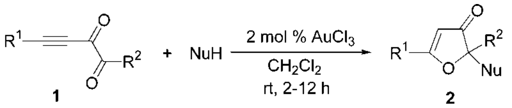
| entry | catalyst | solvent | time (h) | yield of **2a** (%)[a] |
|---|---|---|---|---|
| 1 | 2% $AuCl_3$ | $CH_2Cl_2$ | 3 | 81 |
| 2 | 2% $(PPh_3)AuCl/AgOTf$ | $CH_2Cl_2$ | 3 | 75 |
| 3 | 2% $(PPh_3)AuCl/AgOTf$ | THF | 2 | 84 |
| 4 | 0.1% $AuCl_3$ | $CH_2Cl_2$ | 24 | 69 |
| 5 | 10% AgOTf | $Ch_2Cl_2$ | 12 | n.r.[b] |
| 6 | 10% AgOTf | $(CH_2Cl)_2$ | 12 | n.r.[b,c] |
| 7 | 10% HCl[d] | $CH_2Cl_2$ | 12 | trace |

[a] Isolated yield. [b] n.r. = No reaction. [c] Reaction was carried out at 50 °C. [d] HCl was applied as a 1.8 M solution in ether.

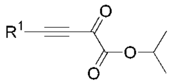
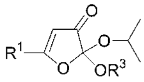
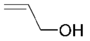
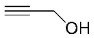
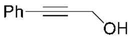
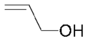
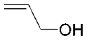
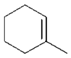
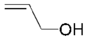
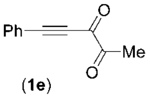
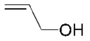
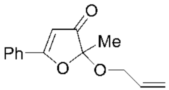
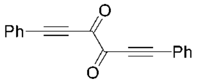
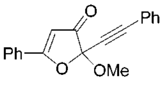
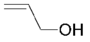
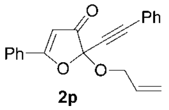
amount of **2a** was observed during the reaction. This result suggested that the gold-based catalysts was responsible for the cyclization. A series of 2-oxo-3-butynoates and 1,2-dicarbonyl compounds such as alkynyl-1,2-diones were subjected to the optimized reaction conditions to react with nucleophiles, and the results are summarized in Table 2.

The alkyne moiety bearing an aromatic ring as well as alkyl substituents all reacted very well to provide the cyclization products in good to high yields. We first investigated the scope of nucleophiles. It was found that, in addition to methanol, a variety of alcohols could be used as effective nucleophiles for this reaction.[17] Treatment of **2a** with ethanol resulted in the formation of **2b** with an ethoxy group in 74% yield (entry 2). When isopropyl alcohol was employed, the corresponding furanone **2c** was formed smoothly in 84% yield. The use of phenol or sterically more hindered alcohol $^t$BuOH also proceeded to afford the cyclized products **2d** and **2e** in 66% and 55% yields, respectively. The reaction of **1a** with allylic alcohol or propargylic alcohol worked well to generate **2f**−**2h** in 68−82% yields (entries 6−8). The procedure is compatible with also alkyl substituted alkynes such as **1b** ($^n$Bu) or **1c** ($^t$Bu) (entries 9 and 10). It is interesting to note that $^t$Bu-substituted alkyne **1c** gave a yield higher than that of **1b** (80 vs 42%). The appearance of a vinylic group in **1d** did not influence the efficiency of this reaction, in which the corresponding products **2l** and **2m** were formed in 76% and 85% yields, respectively (entries 12 and 13). When diketone **1e** was used, the methylated 3(2*H*)-furanone **2n** was obtained in 63% yield. The reaction has been successfully applied to dialkynyl-1,2-diones **1f**, furnishing the products **2o** and **2p** incorporated with an alkynyl group in 88% and 73% yields (entries 15 and 16), respectively. The structure of 3(2*H*)-furanones **2** was supported by extensive NMR experiments (NOESY, COSY, HMQC, and HMBC) of products **2a** and **2h** and further confirmed by single-crystal analysis of **2o**. The results clearly showed five-membered oxygen heterocycles.

**Table 2.** Gold-Catalyzed Construction of 3(2*H*)-Furanones from Activated Alkynes



**1** **2**

| entry | substrate | nucleophile | products | yield(%)[a] |
|---|---|---|---|---|
|  |  | $R^3OH$ |  |  |
| 1 | $R^1$=Ph, (**1a**) | MeOH | **2a** | 81 |
| 2 | (**1a**) | EtOH | **2b** | 74 |
| 3 | (**1a**) | $^i$PrOH | **2c** | 84 |
| 4 | (**1a**) | $^t$BuOH | **2d** | 66 |
| 5 | (**1a**) | PhOH | **2e** | 55 |
| 6 | (**1a**) |  | **2f** | 81 |
| 7 | (**1a**) |  | **2g** | 68 |
| 8 | (**1a**) |  | **2h** | 82 |
| 9 | $R^1$= Bu, (**1b**) |  | **2i** | 42[b] |
| 10 | $R^1$= $^t$Bu, (**1c**) |  | **2j** | 80 |
| 11 | (**1c**) | MeOH | **2k** | 64 |
| 12 |  (**1d**) | MeOH | **2l** | 76 |
| 13 | (**1d**) |  | **2m** | 85 |
| 14 |  (**1e**) |  |  **2n** | 63 |
| 15 |  (**1f**) | MeOH |  **2o** | 88[c] |
| 16 | (**1f**) |  |  **2p** | 73[c] |

[a] Unless noted, all reactions were carried out using 2 mol % of $AuCl_3$ and 1.5 equiv of nucleophile in $CH_2Cl_2$ at room temperature for 2−12 h. [b] The reaction was carried out for 24 h. [c] 3 equiv of nucleophile was used.

On the basis of the above observations, a possible reaction mechanism is proposed in Scheme 2, which may involve the following steps: (i) The alkyne coordinates to $AuCl_3$ as a two-electron ligand to give complex **4**, which enhances the electrophilicity of the alkyne. (ii) The subsequent domino nucleophilic attack/*anti-endo-dig* cyclization affords organogold intermediate **7**. (iii) Protonation of **7** yields 3(2*H*)-furanone **2** and regenerate the catalyst $AuCl_3$. Alternatively, the reaction may involve an oxonium ion **6**,[18] which is formed by the nucleophilic attack of carbonyl oxygen to the gold-coordinated alkynes. The oxonium ion **6** undergoes the

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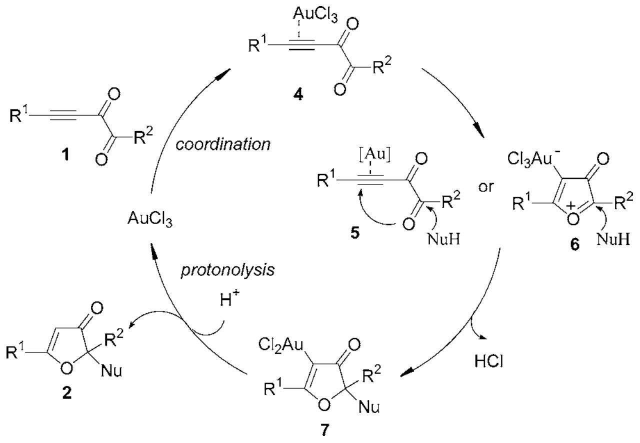
[17] For Ir-catalyzed cyclization/hydroalkoxylation of bis-homopropargylic alcohols to afford cyclic ketals, see: Genin, E.; Antoniotti, S.; Michelet, V.; Genêt, J.-P. *Angew. Chem., Int. Ed.* **2005**, *44*, 4949.

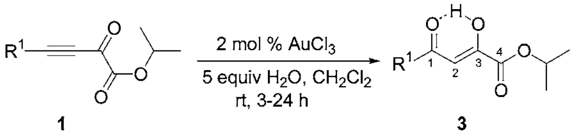
**Scheme 2.** Proposed Reaction Mechanism for Au(III)-Catalyzed Cyclization



subsequent reaction with alcohols followed by protonation to regenerate the Au(III) catalyst and produce the 3(2*H*)-furanone.

On the other hand, hydration of alkynes is one of the most straightforward and environmentally benign routes to form a C−O bond. Several recent papers describe the use of Au(III) ($NaAuCl_4$)[19] and Au(I)[20] catalysts for the addition of water to unactivated alkynes. To probe that $AuCl_3$ could be an effective catalysts for addition of water to these highly activated alkynes, we proceeded to examine the alkyne hydration reactions. Thus, under the conditions depicted in Scheme 3, alkynes **1** reacted with water selectively to form alkene product 2-hydroxy-4-oxo-4-substituted-but-2-enoic ester **3** as a single isomer in 80−88% yields. The structural assignment was supported by detailed analysis of the COSY, HMQC, and HMBC data for **3a**. Strong HMBC correlations between phenyl protons and ketone carbonyl C1 verified the location of the carbonyl group. However, due to a lack of relevant correlations in NOESY spectra, the stereochemistry of double bond could not be defined. The product **3** was suggested to be a (*Z*)-configuration since it might be stabilized by a two-center O···H−O hydrogen bonding.

**Scheme 3.** Gold-Catalyzed Hydration of Alkynes



**3a**, R$^1$=Ph (88%)
**3b**, R$^1$=*p*-MeOC$_6$H$_4$ (80%)
**3c**, R$^1$=$^t$Bu, (83%)

In conclusion, we have succeeded in developing a gold-catalyzed cyclization of 2-oxo-3-butynoates or disubstituted-1,2-diones with various nucleophiles under mild reaction conditions, which provided an efficient and general route to 3(2*H*)-furanones with a wide range of substituents. This is the first report for construction of 3(2*H*)-furanones using transition metal methods. Further studies to elucidate the mechanism of this reaction and to extend the scope of synthetic utility are in progress in our laboratory.

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**Supporting Information Available:** Experimental details and spectroscopic characterization of compounds **2a**−**p** and **3a**−**c** and CIF file giving crystallographic data of **2o**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] For the transition-metal-catalyzed oxonium ion formation, see: (a) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650. (b) Asao, N.; Aikawa, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 7458. (c) Sato, K.; Yudha, S. S.; Asao, N.; Yamamoto, Y. *Synthesis* 2**004**, *9*, 1409. (d) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921. (e) Kusama, H.; Funami, H.; Shido, M.; Hara, Y.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2005**, *127*, 2709. (f) Zhu, J.; Germain, A. R.; Porco, J. A., Jr. *Angew. Chem., Int. Ed.* **2004**, *43*, 1239.

[19] (a) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. *J. Am. Chem. Soc.* **2003**, *125*, 11925. (b) Kukuda, Y.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 3729. (c) Deetlefs, M.; Raubenheimer, H. G.; Esterhuysen, M. W. *Catal. Today* **2002**, *72*, 29. (d) Arcadi, A.; Cerichelli, G.; Chiarini, M.; Di Giuseppe, S.; Marinelli, F. *Tetrahedron Lett.* **2000**, *41*, 9195. (e) Zhou, C.-Y.; Chan, P.; Che, C.-M. *Org. Lett.* **2006**, *8*, 325.

[20] (a) Reference 8l. (b) Mizushima, E.; Sato, K.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4563.