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# Gold-Catalyzed Hydrative Carbocyclization of 1,5- and 1,6-Diyn-3-ones via an Oxygen Transfer Process

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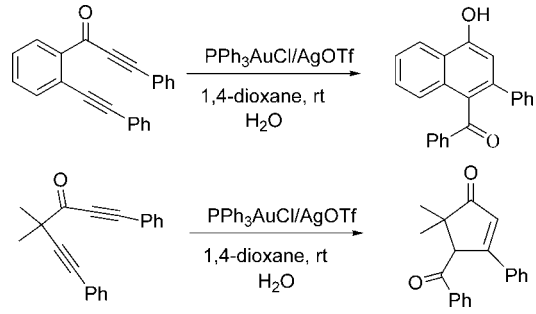
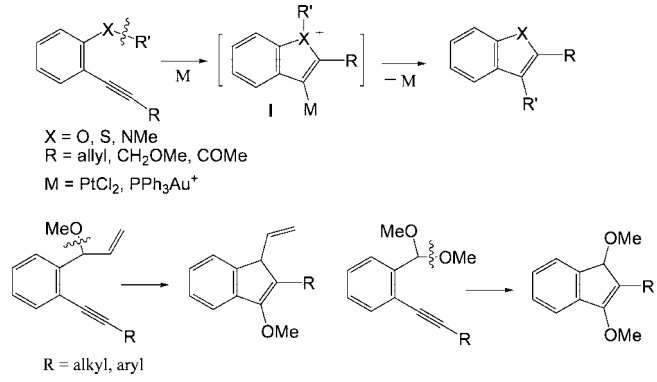



This study reports new hydrative carbocyclizations of 1,5- and 1,6-diyn-3-ones catalyzed by $PPh_3AuOTf$, involving a $\pi$-alkyne-assisted oxygen transfer in the reaction mechanisms. Treatment of 2-(alk-2-yn-1-onyl)-1-alkynylbenzenes with $PPh_3AuOTf$ (5 mol %) in wet 1,4-dioxane (23 °C, 10 min) led to hydrative aromatization to give 4-hydroxyl-1-naphthyl ketones efficiently. This approach is also extendible to the hydrative cyclization of acyclic 1,5-diyn-3-ones, which afforded 4-cyclopentenonyl ketones in reasonable yields. On the basis of this oxygen-labeling study, we propose a plausible mechanism involving an alkyne-assisted oxygen transfer to generate key oxonium and gold-enolate intermediates.

## Introduction

Metal-mediated atom-transfer cyclizations are not only mechanistically interesting, but also synthetically useful to construct complex molecule frameworks.[1,2] One recent impact with gold and platinum catalysis is the cycloizomerization of oxygen-containing alkynylbenzenes via formation of intermediate **I** to complete a transfer of oxygen atom or alkyl fragment; representative examples are provided in Scheme 1.[3,4] The uses of these cyclizations, however, are restricted to the preparation of functionalized indene and five-membered heterocyclic com-

**SCHEME 1. Alkyne-Assisted Fragment Migration**




(1) Reviews: (a) Matyjaszewski, K.; Miller, P. J.; Fossum, E.; Nakagawa, Y. *Appl. Organomet. Chem.* **1998**, *12*, 667. (b) Delaude, L.; Demonceau, A.; Noels, A. F. *Top. Organomet. Chem.* **2004**, *11*, 155. (c) Clark, A. J. *Chem. Soc. Rev.* **2002**, *31*, 1. (d) Byers, J. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: New York, 2001; Vol. 1, pp 72−89. (e) Yet, L. *Tetrahedron* **1999**, *55*, 9349. (f) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 4, pp 779−831.

(2) Selected examples: (a) Cook, G. R.; Hayashi, R. *Org. Lett.* **2006**, *8*, 1045. (b) Yang, D.; Yan, Y.-L.; Zheng, B.-F.; Gao, Q.; Zhu, N.-Y. *Org. Lett.* **2006**, *8*, 5757. (c) Yanada, R.; Koh, Y.; Nishimori, N.; Matsumura, A.; Obika, S.; Mitsuya, H.; Fujii, N.; Takemoto, Y. *J. Org. Chem.* **2004**, *69*, 2417. (d) Yang, D.; Gu, S.; Yan, Y.-L.; Zhu, N.-Y.; Cheung, K.-K. *J. Am. Chem. Soc.* **2001**, *123*, 8612.

(3) (a) Fürstner, A.; Davies, P. W. *J. Am. Chem. Soc.* **2005**, *127*, 15024. (b) Fürstner., A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863. (c) Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785. (d) Nakamura, I.; Sato, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 4473. (e) Shimada, T.; Nakamura, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 10546.

(4) (a) Dubé, P.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 12062. (b) Nakamura, I.; Bajracharya, G. B.; Wu, H.; Oishi, K.; Mizushima, Y.; Gridnev, I. D.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 15423. (c) Nakamura, I.; Bajracharya, G. B.; Mizushima, Y.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 4328.

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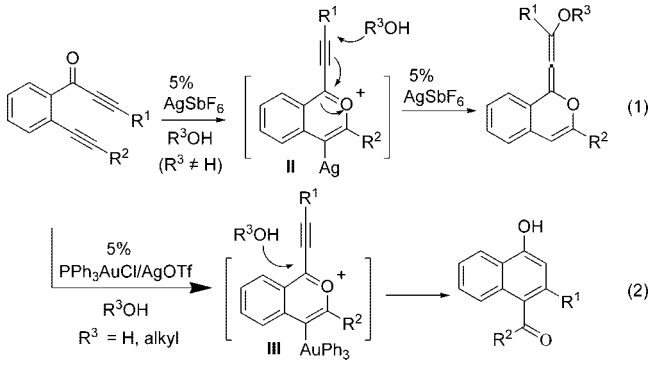
pounds.[1−4] We seek to expand new catalytic reactions involving an oxygen transfer beyond the present scope. Herein we report new hydrative carbocyclizations[5,6] of 2-(alk-2-yn-1-onyl)-1-alkynylbenzenes and acyclic 1,5-diyn-3-ones catalyzed by gold species. These mechanistically interesting reaction represent a transfer of an oxygen atom.

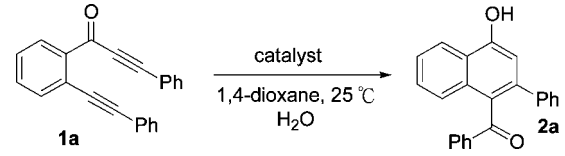
Before this work, Yamamoto reported[8] $AgSbF_6$-catalyzed cyclization of 2-(alk-2-yn-1-onyl)-1-alkynylbenzenes with alcohols in $CH_2Cl_2$, giving benzopyranyl allenes involving formation of silver-benzopyrylium intermediates **II** (eq 1). Although Au(I) resembles Ag(I) in electronic property, the use of $PPh_3AuOTf$ leads to a complete change in the cyclization chemoselectivity of such substrates with water and alcohol, as depicted in eq 2. Herein, formation of 4-hydroxyl-1-naphthyl ketones stems from addition of ROH (R = H, alkyl) at the oxonim of gold-benzopyrylium intermediates **III**.




## Results and Discussions

Table 1 shows our efforts to achieve the hydrative carbocyclization of 2-(alk-2-yn-1-onyl)-1-alkynylbenzenes **1a** over commonly used acid catalysts. $PtCl_2$, $PtCl_2/CO$,[9] AuCl, $AuCl_3$, and $ClAuPPh_3$ (Ph = phenyl), each at 5 mol % loading, led to unreacted **1a** exclusively in wet 1,4-dioxane at 23 °C. Under similar conditions, the use of $AuPPh_3SbF_6$ gave a 69% yield of 4-benzoyl-3-phenyl-1-naphthol **2a**, and the yield was increased to 76% with $PPh_3AuCl/AgOTf$ and a short time reaction (0.8 h). The effect of counteranions is also pronounced for silver salts; $AgSbF_6$ was virtually inactive whereas AgOTf gave a 65% yield of 1-naphthol **2a** with a long reaction period up to 10 h. This reaction time indicates that AgOTf residues did not cause catalytic activity of $AuPPh_3OTf$. In dry 1,4-dioxane, all these acid catalysts including $PPh_3AuOTf$ gave an exclusive recovery of starting diynone **1a** without cycloizomerization. Characterization of the molecular structure of compound **2a** relies on an X-ray diffraction study of its related compound **2g** (Table 2, entry 7).[10]

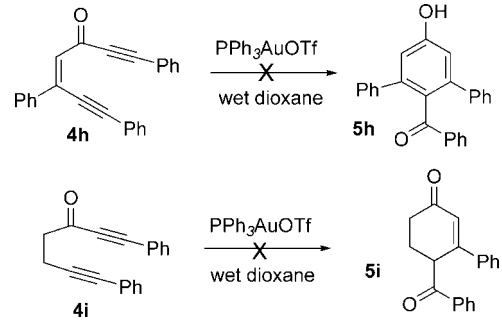
**TABLE 1. Catalytic Cyclization over Various Catalysts**




| catalyst[a] | time(h) | products[b] 1a (%) | products[b] 2a (%) |
|---|---|---|---|
| (1) $PtCl_2$ | 15 | 97 | - |
| (2) $PtCl_2/CO$ | 15 | 95 | - |
| (3) AuCl | 15 | 88 | 5 |
| (4) $AuCl_3$ | 15 | 72 | 13 |
| (5) $PPh_3AuCl$ | 15 | 97 | - |
| (6) HOTf | 24 | 90 | - |
| (7) $PPh_3AuCl/AgSbF_6$ | 6 | - | 69 |
| (8) $PPh_3AuCl/AgOTf$ | 0.8 | - | 75 |
| (9) $AgSbF_6$ | 15 | 93 | - |
| (10) AgOTf | 10 | - | 65 |
| (11) $PPh_3AuCl/AgOTf$[c] | 48 | 82 | 3 |

[a] 5 mol % catalyst, [diynone] = 0.1 M, $H_2O$ (5 equiv) for entries 1−10. [b] Products are separated from silica column. [c] No water was added.

The preceding catalysis provides a new and facile synthesis of highly functionalized 1-naphthol from easily prepared 2-(alk-2-yn-1-onyl)-1- alkynylbenzenes. We prepared various ketones **1a**−**o** with alterations of the $R^1$, $R^2$, $R^3$, and $R^4$ substituents to demonstrate the generality of this new cyclization. Substrates **1a**−**c** bearing a phenylethynyl group ($R^1$ = phenyl, entries 1−3) are much more efficient than their hexynyl analogues **1d**−**f** ($R^1$ = *n*-Bu, entries 4−6) in this hydrative cyclization upon comparison of their respective product yields and reaction periods. This cyclization is very suitable for substrates **1g**−**i** with alterations of their $R^1$ substituent with 3,5-dimethylphenyl, 4-fluorophenyl, 4-and methoxyphenyl (entries 7−9), but it becomes inefficient with species **1j** bearing a 4-trifluoromethylphenyl group (entry 10). Entries 11−15 show the effects of




(5) For Ru catalysts, see selected examples: (a) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2003**, *125*, 11516. (b) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2005**, *127*, 4763. (c) Odedra, A.; Wu, C.-J.; Pratap, T. B.; Huang, C.-W.; Ran, Y. F.; Liu, R.-S. *J. Am. Chem. Soc.* **2005**, *127*, 3406. (d) Trost, B. M.; Brown, R. E.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 5877.

(6) For gold and platinum catalysts, see the following examples: (a) Kennedy-Smith, J. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 4526. (b) Yang, C.-Y.; Lin, G.-Y.; Liao, H.-Y.; Datta, S.; Liu, R.-S. *J. Org. Chem.* **2008**, *73*, 4907. (c) Chang, H.-K.; Datta, S.; Das, A.; Odedra, A.; Liu, R.-S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4744. (d) Das, A.; Liao, H.-H.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 9214. (e) Chang, H.-K.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 8139. (f) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 4160. (g) Jin, T.; Yamamoto, Y. *Org. Lett.* **2007**, *9*, 5259.

(7) For palladium catalyst, see Momiyama, N.; Kanan, M. W.; Liu, D. R. *J. Am. Chem. Soc.* **2007**, *129*, 2230.

(8) Patil, N. T.; Pahadi, N. K.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 10096.

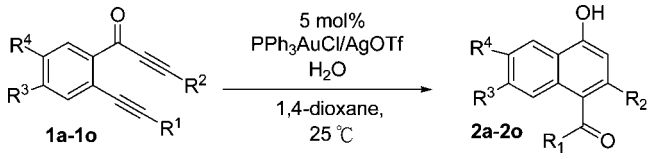
(9) For $PtCl_2/CO$ catalysts, see the following selected examples: (a) Fürstner, A.; Davies, P. W.; Gress, T. *J. Am. Chem. Soc.* **2005**, *127*, 8244. (b) Zhang, G.; Catalano, V. J.; Zhang, L. *J. Am. Chem. Soc.* **2007**, *129*, 11358. (c) Taduri, B. P.; Ran, Y.-F.; Huang, C.-W.; Liu, R.-S. *Org. Lett.* **2006**, *8*, 883. (d) Lo, C.-Y.; Lin, C.-C.; Cheng, H.-M.; Liu, R.-S. *Org. Lett.* **2006**, *8*, 3153.

(10) The X-ray data of compound **2g** are provided in the Supporting Information.

(11) Treatment of acyclic 1,6-diyn-3-ones **4h** and **4i** with $PPh_3AuOTf$ in wet 1,4-dioxane did not give the desired cyclized ketones **5h** and **5i**, but a messy mixture of products. Spectral data of ketone substrates **4h** and **4i** were provided in the Supporting Information.

(12) The complete mass spectra of $^{18}O$-enriched **1a** and **2a** are provided in the Supporting Information.

**TABLE 2. Gold-Catalyzed Hydrative Cyclization of Aromatic 1,6-Diyne-3-ones**



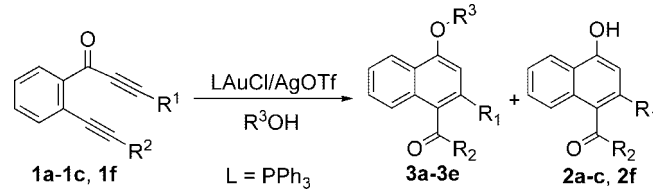

| | substrate[a] | time (h) | |
|---|---|---|---|
| | $R^1$ = Ph, $R^3$ = $R^4$ = H | | |
| 1 | $R^2$ = Ph (**1a**) | 0.8 | **2a** (75) |
| 2 | $R^2$ = Me (**1b**) | 1.0 | **2b** (59) |
| 3 | $R^2$ = $^n$Bu (**1c**) | 1.0 | **2c** (73) |
| | $R^1$ = $^n$Bu, $R^3$ = $R^4$ = H | | |
| 4 | $R^2$ = $^n$Bu (**1d**) | 16 | **2d** (45) |
| 5 | $R^2$ = Me (**1e**) | 24 | **2e** (32) |
| 6 | $R^2$ = Ph (**1f**) | 24 | **2f** (38) |
| | $R^2$ = Me, $R^3$ = $R^4$ = H | | |
| 7 | $R^1$ = 3,5-$Me_2C_6H_3$ (**1g**) | 0.5 | **2g** (61) |
| 8 | $R^1$ = 4-$FC_6H_4$ (**1h**) | 1.0 | **2h** (63) |
| 9 | $R^1$ = 4-$MeOC_6H_4$ (**1i**) | 0.5 | **2i** (72) |
| 10 | $R^1$ = 4-$CF_3C_6H_4$ (**1j**) | 24 | **2j** (23) |
| | $R^1$ = Ph, $R^2$ = Me | | |
| 11 | $R^3$ = H, $R^4$ = OMe (**1k**) | 1.0 | **2k** (82) |
| 12 | $R^3$ = H, $R^4$ = F (**1l**) | 1.0 | **2*l*** (93) |
| 13 | $R^3$ = OMe, $R^4$ = H (**1m**) | 24 | **2m** (11) |
| 14 | $R^3$ = F, $R^4$ = H (**1n**) | 1.0 | **2n** (93) |
| 15 | $R^3$ = Cl, $R^4$ = H (**1o**) | 1.0 | **2o** (75) |

[a] [Substrate] = 0.1 M, $H_2O$ (5 equiv), 1 h. [b] Products are separated by silica gel column chromatography.

the phenyl $R^3$ and $R^4$ substituents of diynones **1k**−**o**, and their cyclizations maintain high efficiencies except for compound **1m** bearing a $R^3$ = OMe group.

This gold catalysis is also compatible with alcohol nucleophiles with examples provided in Table 3. Treatment of 1,6-diyn-3-one **1a** with isobutanol (3 equiv) and $PPh_3AuOTf$ catalyst (5 mol %) in dry 1,4-dioxane produced 1-benzoyl-4-isobutoxynaphthalene **3a** in 54% yield together with a small quantity of 1-naphthol **2a** (8%); the yield of undesired species **2a** was further increased to 28% in wet 1,4-dioxane (entry 2). We only

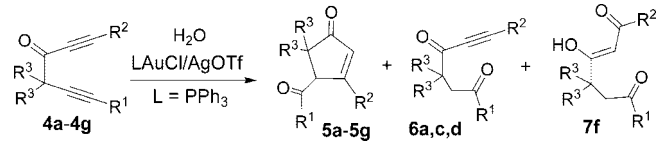
**TABLE 3. Gold-Catalyzed Cycliction of Diynone with Alcohol**




| entry | substrate | $R^3$ | $H_2O$ (equiv) | time (h) | product[a] (yield[b]) |
|---|---|---|---|---|---|
| 1 | $R^1$ = $R^2$ = Ph (**1a**) | *i*-Bu | | 2 | **3a** (54%), **2a** (8%) |
| 2 | **1a** | *i*-Bu | 5 | 2 | **3a** (34%), **2a** (28%) |
| 3 | **1a** | Me | | 2 | **3b** (60%) |
| 4 | $R^1$ = Me, $R^2$ = Ph (**1b**) | Me | | 2 | **3c** (59%), **2b** (17%) |
| 5 | $R^1$ = Bu, $R^2$ = Ph (**1c**) | Me | | 2 | **3d** (55%), **2c** (10%) |
| 6 | $R^1$ = Ph, $R^2$ = $^n$Bu (**1f**) | Me | | 4 | **3e** (58%), **2f** (16%) |

[a] [Substrate] = 0.1 M, dioxane, alcohol (5 equiv), 25 °C. [b] Products are separated by silica gel column chromatography.

**TABLE 4. Gold-Catalyzed Hydrative Carbocyclization of Acyclic 1,5-Diyn- 3-ones**




| | substrate[a] | | | |
|---|---|---|---|---|
| entry | $R^1$ | $R^2$ | time (h) | products[b] (yields) |
| | | $R^3$ = Me | | |
| (1) | Ph | Ph (**4a**) | 2 | **5a** (45%), **6a** (17%) |
| (2) | Ph | Me (**4b**) | 2 | **5b** (53%) |
| (3) | Ph | Bu (**4c**) | 2 | **5c** (48%) |
| | | $R^3$, $R^3$ = $(CH_2)_5$ | | |
| (4) | Ph | Ph (**4d**) | 2 | **5d** (38%), **6d** (27%) |
| (5) | Ph | Me (**4e**) | 0.5 | **5e** (57%) |
| (6) | 4-$FC_6H_4$ | Ph (**4f**) | 0.5 | **5f** (55%), **7f** (13%) |
| (7) | 4-$FC_6H_4$ | Me (**4g**) | 0.5 | **5g** (73%) |

[a] Conditions: 5 mol % catalyst, 2 equiv of $H_2O$, 0.2 M dry dioxane, 25 °C. [b] Products are separated by silica gel column chromatography.

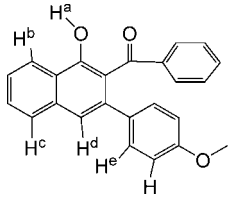
obtained cyclized product **3b** in 60% yield in dry 1,4-dioxane when MeOH was used as the nucleophile. This nucleophilic aromatization was extendible to other 1,6-diyn-3-ones **1b**−**c** and **1f**, which gave 4-methoxy-1-naphthyl ketone products **3c**,**d** in 55−59% yields in addition to minor side products **2b**, **2c**, and **2f**. The proposed structure of compound **3b** was verified because it was also produced from the reaction of 1-naphthol **2a** with MeI and NaH in THF.

We also prepared acyclic 1,5-diyn-3-one substrates **4a**−**g** to expand the scope of this hydrative carbocyclization, as depicted in Table 4. Treatment of these substrates with $PPh_3AuCl/AgOTf$ (5 mol %) in wet 1,4-dioxane (25 °C) delivered 4-cyclopentenonyl ketone products **5a**−**g** in reasonable yields (38−73%). To attain a smooth cyclization, the alkynyl $R^1$ substituents of these substrates are strictly limited to phenyl groups whereas their $R^2$ groups tolerate either alkyl or phenyl groups; such a structure−activity pattern parallels that of aromatic diynones **1a**−**f** (entries 1−6, Table 2). In such reactions, we also obtained side products **6a**, **6d**, and **7f** in minor proportions (13−27%), produced from gold-catalyzed alkyne hydration. Subsequent treatment of **6a** and **7f** with the same gold catalyst in wet 1,4-

(13) Reviews for benzopyrilium see: (a) Asao, N. *Synlett* **2006**, *11*, 1645. (b) Kuznetsov, E. V.; Shcherbakova, I. V.; Balaban, A. T. *Adv. Heterocycl. Chem.* **1990**, *50*, 157.

(14) For metal catalysis involving benzopyrylium as reaction intermediates, see: (a) Beeler, A. B.; Su, S.; Singleton, C. A.; Porco, J. A., Jr. *J. Am. Chem. Soc.* **2007**, *129*, 1413. (b) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650. (c) Asao, N.; Aikawa, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 7458. (d) Nakamura, I.; Mizushima, Y.; Gridnev, I. D.; Yamamoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 9844. (e) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814.

(15) Spectral data of compounds **8** and **9** are provided in the Supporting Information. Structural assignment of compound **9** was determined by $^1H$ NOE-effect with the map shown below. The hydroxyl proton has a proton signal at $\delta$ 11.7, which disappeared upon treatment with $CD_3OD$ in hot $CDCl_3$ (60 °C, 2 h).




| irradiation | enhancement (%) |
|---|---|
| $H^a$ ($\delta$ 11.7) | $H^b$ ($\delta$ 8.46, 1.92%) |
| $H^c$ ($\delta$ 7.80) | $H^d$ ($\delta$ 7.32, 7.75%) |
| $H^e$ ($\delta$ 7.11) | $H^d$ ($\delta$ 7.32, 8.11%) |

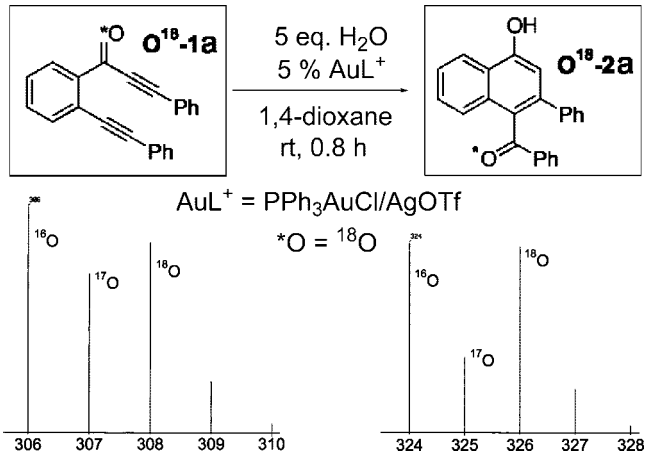
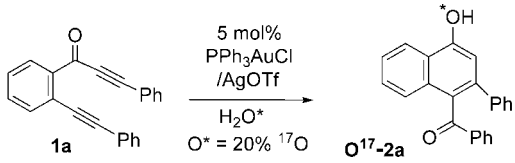



**FIGURE 1**

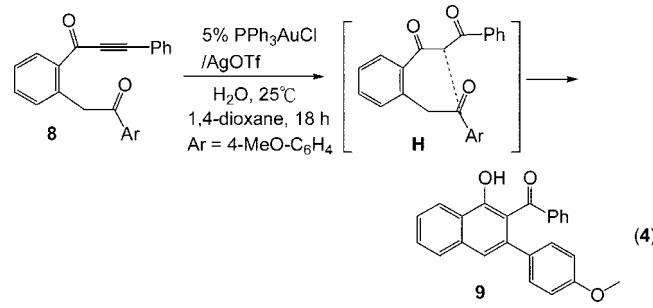
dioxane (25 °C) failed to give major cyclized products **5a** and **5f**; these minor products were not intermediates for desired cyclopentenonyl ketones. We were unsuccessful in obtaining 4-cyclohexenonyl ketone products through hydrative cyclization of acyclic 1,6-diyn-3-ones under similar conditions.[11]

We performed a $^{17}O$-labeling experiment to elucidate the mechanism of the hydrative cyclization. Treatment of aromatic 1,6-diyn-3-one **1a** with $H_2{}^{17}O$ and $PPh_3AuOTf$ (5 mol %) in 1,4-dioxane provided $^{17}O$-**2a**, which showed a broad peak ($\delta$ 75 ppm) assignable to the phenoxy oxygen. We did not observe any C=$^{17}O$ signal of species $^{17}O$-**2a** in the in situ NMR study, or from the purified $^{17}O$-**2a** sample by flash chromatography. This isotopic labeling experiment provides results compatible with our observation for the alcohol-based aromatization (see Table 3). In a separate experiment, we also prepared $^{18}O$-**1a** bearing a ca. 45% $^{18}O$ enrichment at the carbonyl oxygen, and its $PPh_3AuOTf$-catalyzed cyclization with natural $H_2O$ (5.0 equiv) afforded the cyclized product $^{18}O$-**2a**, which retained a significant amount of $^{18}O$-content at the ketone group ($\upsilon_{CO^{16}}$ = 1655 cm$^{-1}$; $\upsilon_{CO^{18}}$ = 1620 cm$^{-1}$) upon comparison of their respective mass parent peaks (Figure 1).[12] The small peak at 327 of compound $^{18}O$-**2a** is assignable to the M + 1 peak of $^{18}O$-embedded **2a**, and we did not obtain a clear peak at 328 assignable to a incorporation of two $^{18}O$-atoms.




(3)

On the basis of oxygen labeling experiments, we propose a plausible mechanism in Scheme 2, which involves benzopyrylium **B** as the reaction intermediate.[13,14] We believe that the cyclization efficiency of this catalysis depends on the state of the equilibrium of **A** and **A′**. This hypothesis also rationalizes the observation that a 4-methoxyphenyl group greatly decreases the cyclization efficiency (Table 2, entry 13) because it increases the ketone basicity to favor $\sigma$-bonded ketone **A′**. Once the benzopyrylium **B** is formed, its oxonium group is subject to the attack of water to form cyclic ketal species **C**. A subsequent proton-catalyzed opening of this ketal species generates gold enol form **D**, which subsequently produces ketone form **D′**. We believe that the Bronsted acid catalyzes the ketone−enol equilibrium, and a subsequent attack of the enol group of species **D** on the proton-coordinated alkynone in a Michael-type reaction will give cyclohexenone **E**, which ultimately forms observed product **2a**. This proposed mechanism also rationalizes the formation mechanism of 4-cyclopentenonyl ketone **5a** from acyclic 1,5-diyn-3-one **4a**, which includes similar gold enolate **F** and gold cyclopentenonyl intermediate **G**. As depicted in eq 4, gold-free ketone species **8** (Ar = 4-MeO-$C_6H_4$) is unlikely to be an intermediate for 2-naphthol product because it led to different aromatization compound **9** catalyzed by $PPh_3AuCl$/AgOTf under reaction conditions according to our control experiment.[15] This information supports the proposed conversion of gold-enolate **F** to gold-cyclohexenonyl species **G**.



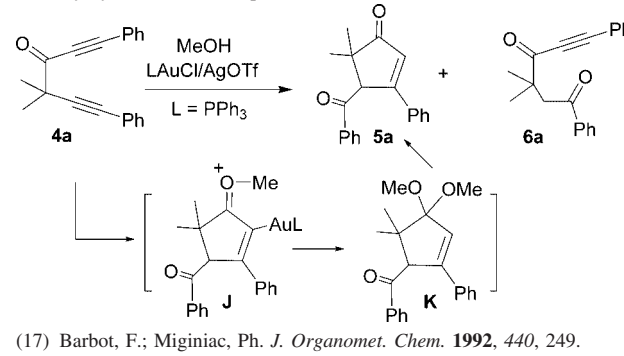

(4)

This proposed mechanism also provides rationales for the high efficiencies for diynones **1a**−**c** bearing an arylethynyl group ($R^1$ = aryl), which are more efficient than their hexynyl analogues **1d**−**f** ($R^1$ = *n*-Bu), as depicted in Table 2 (entries 1−6). We envisage that the aryl group of $\pi$-alkyne species **A** stabilizes the vinyl cationic resonance (Scheme 3) to facilitate the formation of benzopyrylium **B**. The oxygen labeling experiments also exclude the possibility that hydrated ketone species **I** is responsible for formation of cyclic ketal intermediate **C**, which is expected to give cyclized product with the $^{17}O$-labeling at both the ketone and phenol groups.

## Conclusion

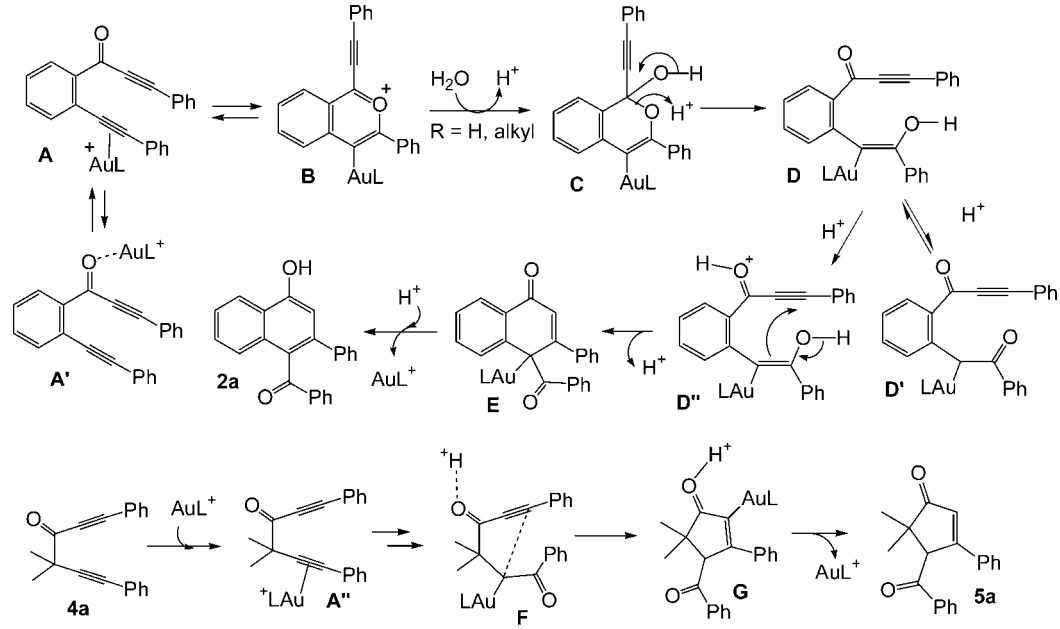
In this investigation, we report the use of $PPh_3AuOTf$ to implement hydrative carbocyclization of 2-(alk-2-yn-1-onyl)-1-alkynylbenzenes and acyclic 1,5-diyn-3-ones under ambient conditions, providing 4-ketonyl-1-naphthols and cyclopentenyl ketones, respectively. The mechanisms of these reactions have been studied by oxygen-labeling and suitable control experiments; we propose that such hydrative carbocyclizations proceed through an alkyne-assisted oxo transfer to generate gold-containing oxonium and enolate intermediates to complete the cyclization.[16]

(16) (a) Treatment of 1,5-diyn-3-one **4a** with MeOH (2 equiv) and $PPh_3AuCl$/AgOTf (5 mol %) in dry dioxane (25 °C, 4h) gave 4-cyclopentenonyl ketone **5a** and **6a** in 46% and 28% yields, respectively. Formation of ketone **5a** is probably due to easy hydration of ketal speices **J**.

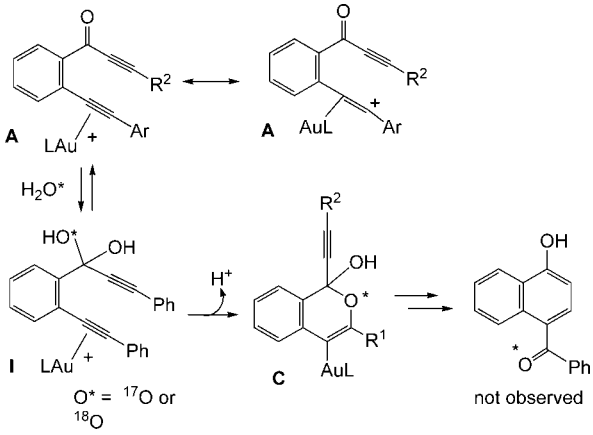



(17) Barbot, F.; Miginiac, Ph. *J. Organomet. Chem.* **1992**, *440*, 249.

**SCHEME 2. A Plausible Mechanism for the Hydrative Carbocyclization Reaction**



**SCHEME 3. A Proposed Mechanism to Rationalize $^{18}$O-Labeling Results**



## Experimental Sections

**General Sections.** Synthesis of aromatic 1,6-diyne-3-ones has been previously reported in the literature.[8] 2,2-Dimethylbut-3-yn-1-ol was prepared according to literature procedure.[17] $^1$H NMR spectra were run at 600 and 400 MHz and $^{13}$C NMR experiments were operated at 125 and 100 MHz in $CDCl_3$ or $CD_2Cl_2$ solution.

**Experimental Procedure for Cyclization of 1,6-Diyne-3-one (1a) to 2-Naphthol Derivative (2a).** A flask containing $AuClPPh_3$ (8.0 mg, 0.016 mmol) and AgOTf (4.2 mg, 0.016 mmol) was charged with dioxane (0.26 mL) and the mixture was stirred for 2 min. To this mixture was added diynone **1a**[8] (100 mg, 0.326 mmol) and $H_2O$ (29.3 mg, 1.63 mmol) in dioxane (3 mL). After complete consumption of starting diynone **1a**, the solution was evaporated to dryness, and the residues were eluted through a short silica column (hexane/ethyl acetate: 5/1) to afford 1-naphthyl ketone **2a** (79.7 mg, 0.244 mmol, 75%) as a yellow oil. IR (nujol, cm$^{-1}$): 3310 (br s), 3012 (s), 1652 (m), 1643 (m), 1251 (s); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.25 (dd, $J$ = 7.5, 1.4 Hz, 1H), 7.69 (dd, $J$ = 7.4, 0.9 Hz, 1 H), 7.58 (dd, $J$ = 8.1, 1.0 Hz, 2 H), 7.48−7.40 (m, 2 H), 7.34 (tt, $J$ = 7.4, 1.5 Hz, 1 H), 7.25−7.16 (m, 5 H), 7.13−7.09 (m, 2 H), 6.83 (s, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 200.1, 152.0, 140.1, 138.6, 138.4, 133.0, 132.2, 129.6 (2 × CH), 129.2 (2 × CH), 128.3, 128.1 (2 × CH), 128.0 (2 × CH), 127.7, 127.3, 125.4, 125.2, 123.4, 122.0, 110.1; HRMS calcd for $C_{23}H_{16}O_2$ 324.1150, found:324.1152.

**Experimental Procedure for Cyclization of 4,4-Dimethyl-1,6-diphenylhexa-1,5-diyn-3-one (4a) to 4-Benzoyl-5,5-dimethyl-3-phenylcyclopent-2-enone (5a) and 3,3-Dimethyl-1,6-diphenylhex-5-yne-1,4-dione (6a).** A flask containing $AuClPPh_3$ (9.0 mg, 0.018 mmol) and AgOTf (4.7 mg, 0.018 mmol) was charged with dioxane (0.26 mL) and the mixture was stirred for 2 min. To this solution was added diynone **4a** (100 mg, 0.367 mmol) and $H_2O$ (13.2 mg, 0.73 mmol) in dioxane (0.73 mL). After consumption of starting diynone **4a**, the solution was evaporated to dryness, and the residues were purified by column chromatography (hexane/ethyl acetate: 5/1) to yield cyclopentenone **5a** (47.8 mg, 0.165 mmol, 45%) and diketone **6a** (18.1 mg, 0.062 mmol, 17%).

**5a:** colorless oil; IR (nujol, cm$^{-1}$) $\nu$ 1670 (s), 1607 (s), 1701 (s), 1603 (s); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.04 (dd, $J$ = 6.8, 1.6 Hz, 2 H), 7.65 (tt, $J$ = 7.4, 1.2 Hz, 1 H), 7.55 (dd, $J$ = 7.9, 0.6 Hz, 2 H), 7.47−7.44 (m, 2 H), 7.36−7.29 (m, 3 H), 6.72 (s, 1 H), 5.12 (s, 1 H), 1.42 (s, 3 H), 0.94 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 211.1, 197.9, 170.0, 137.4, 133.8, 133.2, 131.0, 129.1 (2 × CH), 128.9 (2 × CH), 128.4 (2 × CH), 127.2, 127.0 (2 × CH), 59.7, 48.1, 27.3, 20.6. HRMS calcd for $C_{20}H_{18}O_2$ 290.1307, found 290.1304.

**6a:** pale yellow oil;. IR (nujol, cm$^{-1}$) $\nu$ 2157 (w), 1692 (s), 1672 (s), 1605 (s); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.94 (dd, $J$ = 8.0, 1.2 Hz, 2 H), 7.53 (d, $J$ = 7.5 Hz, 1 H), 7.50−7.48 (m, 2 H), 7.43−7.37 (m, 3 H), 7.32 (td, $J$ = 7.2, 1.4 Hz, 2 H), 3.44 (s, 2 H), 1.40 (s, 6 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 197.3, 192.5, 136.9, 133.1, 132.9 (2 × CH), 130.4, 128.5 (2 × CH), 128.5 (2 × CH), 128.0 (2 × CH), 120.3, 92.2, 85.8, 48.1, 46.2, 24.9 (2 × $CH_3$). HRMS calcd for $C_{20}H_{18}O_2$ 290.1307, found 290.1309.

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**Supporting Information Available:** Experimental procedures for the synthesis of reaction substrates and catalytic operations, NMR spectra, spectral data of compounds **1a**−**7f**, **8**, and **9**, and X-ray structural data of compound **2g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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