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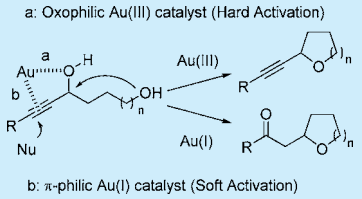
Gold(I)/(III)-Catalyzed Synthesis of Cyclic Ethers; Valency-Controlled Cyclization Modes

Nobuyoshi Morita,* Arisa Yasuda, Motohiro Shibata, Shintaro Ban, Yoshimitsu Hashimoto, Iwao Okamoto, and Osamu Tamura*

Showa Pharmaceutical University, Machida, Tokyo, 194-8543, Japan

Supporting Information

ABSTRACT: Strategic use of oxophilic (hard) gold(III) and π-philic (soft) gold(I) catalysts provides access to two types of cyclic ethers from propargylic alcohols. Thus, heating propargylic alcohols with an oxophilic gold(III) catalyst ($AuBr_3$) results in cyclization to afford cyclic ethers bearing an acetylenic moiety, due to coordination of gold(III) to the oxygen of the propargylic hydroxyl group. On the other hand, propargylic alcohols with a π-philic gold(I) catalyst ($Ph_3PAuNTf_2$) induces Meyer−Schuster rearrangement to afford α,β-unsaturated ketones, which undergo gold(III)-catalyzed intramolecular oxa-Michael addition to afford cyclic ethers bearing a carbonyl group, due to coordination of gold(III) to the oxygen of the carbonyl group.



Gold catalysts were initially recognized as π-acidic catalysts that activate unsaturated bonds, such as alkynes, allenes, and alkenes, for nucleophilic attack to form C−C, C−O, C−N, and C−S bonds.[1] Later, groups led by Gevorgyan[2b] and Campagne[3c] reported the oxophilic character[4] of gold(III) catalysts, which efficiently activate oxygen functionalities even in the presence of an unsaturated bond (allene/alkyne). Since then, nucleophilic substitution reactions of benzyl alcohols[5] or their acetates[6] via oxophilic gold(III)-catalyzed activation of the hydroxyl or acetoxy group have been reported. We rationalized these observations in terms of the hard and soft acids and bases (HSAB) principle, which states that metal ions in low valence states exhibit soft character, whereas metal ions in high positive oxidation states show hard character.[7,8] Thus, gold(I) catalysts may behave as soft acids and gold(III) catalysts as hard acids. On the basis of this working hypothesis, we designed synthetic methods to obtain two types of cyclic ethers from the same propargyl alcohols by means of valency-controlled gold-catalyzed regiodivergent activation (Figure 1). Here, we report an oxophilic (hard) gold(III)-catalyzed cyclization of propargylic alcohols (route A, Figure 1) and a π-philic (soft) gold(I)-catalyzed Meyer−Schuster rearrangement[9,10] followed by oxophilic (hard) gold(III)-catalyzed oxa-Michael addition[11,12] (route B, Figure 1). Thus, strategic use of the two gold catalysts enables diversity-oriented synthesis of two types of cyclic ethers.

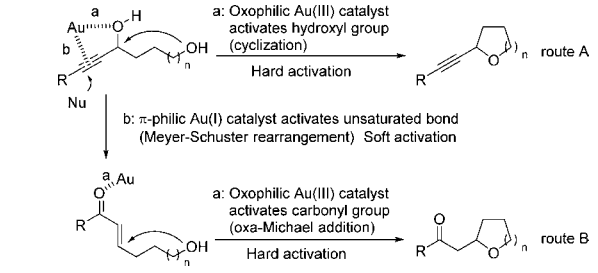
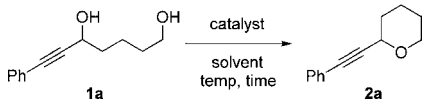


Figure 1. Our strategy for using gold(I)/(III) catalysts.

We first examined cyclization of the propargylic alcohol (route A, Figure 1) by using alcohol **1a** as a model substrate with small amounts of a gold(III) catalyst (Table 1). Thus, treatment of **1a** with 5 mol % of $AuBr_3$ or $HAuCl_4{\cdot}3H_2O$ induced cyclization to furnish cyclic ether **2a** bearing an acetylenic moiety in good yield (entries 1 and 2). Optimization of the reaction conditions was carried out with propargylic alcohol **1a** using gold(III) catalysts. Higher temperature dramatically accelerated the reaction. On heating propargylic alcohol **1a** with 5 mol % of the gold(III) catalyst, $AuBr_3$ or $HAuCl_4{\cdot}3H_2O$, in refluxing $ClCH_2CH_2Cl$

Table 1. Optimization of Reaction Conditions with Gold(III) Catalyst



1a **2a**

entry	catalyst (mol %)	solvent	temp	time	yield
1	$AuBr_3$ (5)	CH_2Cl_2	rt	4 h	63%
2	$HAuCl_4{\cdot}3H_2O$ (5)	CH_2Cl_2	rt	4 h	64%
3	$AuBr_3$ (5)	DCE	reflux	5 min	80%
4	$HAuCl_4{\cdot}3H_2O$ (5)	DCE	reflux	5 min	80%
5[a]	$AuBr_3$ (5)	DCE	reflux	5 min	73%
6	$AuBr_3$ (5)/$AgNTf_2$ (15)	DCE	reflux	5 min	83%
7	$AgNTf_2$ (5)	DCE	reflux	5 min	40%

[a]The reaction was carried out at high concentration (0.73 M). DCE = $ClCH_2CH_2Cl$.

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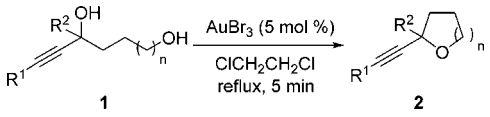
(DCE), the reaction was completed within 5 min to give cyclic ether **2a** in 80% yield (entries 3 and 4). To generate a cationic gold catalyst, a silver catalyst ($AgNTf_2$) was used as cocatalyst in the reaction (entry 6). The system of $AuBr_3$ (5 mol %) and $AgNTf_2$ (15 mol %) was found to slightly increase the yield of the desired product **2a**. On the other hand, we found that $AgNTf_2$ (5 mol %) alone as well as $AuBr_3$ (5 mol %) was capable of catalyzing the cyclization, but with a significantly low yield (entry 3 vs 7). It is noteworthy that treatment of **1a** at high concentration (0.73 M solution) with 5 mol % of $AuBr_3$ provided cyclic ether **2a** in 73% yield without dimer formation (entry 5), even though a gold(III)-catalyzed intermolecular ether formation of phenyl acetylenic carbinol with ethanol at even lower concentration (0.2 M) has been reported.[3b] In contrast, other transition metal catalysts or Lewis acids, such as $Sc(OTf)_3$, CuI, and $BF_3{\cdot}OEt_2$, afforded no cyclized product.

We next investigated the effect of substituents at the alkyne terminus of propargylic alcohols **1b–f** on the cyclization; we chose $AuBr_3$ as the gold(III) catalyst because it is less hygroscopic than $HAuCl_4{\cdot}3H_2O$ (Table 2). Alkyne-terminal

Table 2. $AuBr_3$-Catalyzed Cyclization of Various Propargylic Alcohols 1



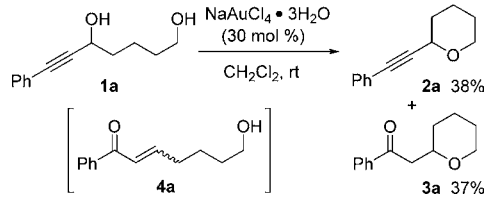
1 2

entry	1	R^1	R^2	n	additive (mol %)	2	yield
1	**1b**	*t*-Bu	H	2	none	**2b**	60%
2	**1b**	*t*-Bu	H	2	$AgNTf_2$ (15)	**2b**	22%
3	**1c**	*n*-Hex	H	2	none	**2c**	18%
4	**1c**	*n*-Hex	H	2	$AgNTf_2$ (15)	**2c**	60%
5	**1d**	*c*-Hex	H	2	$AgNTf_2$ (15)	**2d**	50%
6	**1e**	H	H	2	none	**2e**	not detected
7	**1f**	Ph	Me	2	none	**2f**	52%
8	**1g**	Ph	H	1	none	**2g**	80%
9	**1h**	Ph	H	3	none	**2h**	46%

substituents influenced cyclization of propargylic alcohols **1b–f**. Propargylic alcohol **1b** bearing a *tert*-butyl group with $AuBr_3$ (5 mol %) was smoothly transformed to the corresponding product **2b** in good yield (entry 1), but the cationic gold catalyst generated by $AuBr_3$ (5 mol %) and $AgNTf_2$ (15 mol %) with alcohol **1b** afforded product **2b** in low yield along with many unidentified products (entry 2). On the other hand, treatment of propargylic alcohol **1c** having an *n*-hexyl group with $AuBr_3$ (5 mol %) furnished the corresponding product **2c** in low yield (entry 3), while the system of $AuBr_3$ (5 mol %) and $AgNTf_2$ (15 mol %) smoothly catalyzed cyclization of alcohol **1c** to give the product **2c** in good yield (entry 4). Propargylic alcohol **1d** also underwent cyclization, affording the corresponding product **2d** in moderate yield (entry 5). The reaction of alcohol **1e** with a terminal alkyne gave no cyclized product **2e** (entry 6). Tertiary propargyl alcohol **1f** was efficiently converted into the corresponding cyclic ether **2f** in good yield (entry 7). To our delight, this cyclization was found to be effective for construction of five- and seven-membered cyclic ethers, as well as six-membered ones (entries 8 and 9). Thus, propargylic alcohols **1g** and **1h** reacted under similar conditions to those used for **1a–f** to afford five- and seven-membered ring products **2g** and **2h** in 80% and 46% yields, respectively. This is the first noble metal-catalyzed cyclization of propargyl alcohols that is available for five- to seven-membered rings. The transformation of **1** to **2** is reminiscent of the Nicholas reaction.[13] However, the overall process using the Nicholas reaction would require at least three steps: complexation of **1** with a stoichiometric amount of $Co_2(CO)_8$, treatment of the resulting complex with a Lewis acid for cyclization, and decomplexation of the alkyne–dicobalt complex with a stoichiometric amount of oxidizing reagent. In contrast, the present cyclization offers several advantages: (1) one-step transformation of **1** to **2**, (2) rapid cyclization within 5 min, (3) only a catalytic amount of $AuBr_3$ is required, and (4) H_2O is the only byproduct.

During optimization of reaction conditions for gold(III)-catalyzed cyclization with propargylic alcohol **1a**, we surprisingly found that use of 30 mol % of $NaAuCl_4{\cdot}3H_2O$ in CH_2Cl_2 afforded cyclic ether **2a** in 38% yield along with another cyclic ether **3a** having a carbonyl group in 37% yield (Scheme 1). Formation of **3a** may be rationalized by postulating intramolecular oxa-Michael addition of α,β-unsaturated ketone **4a** produced by Meyer–Schuster rearrangement of **1a**.

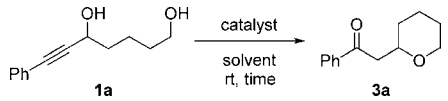
Scheme 1. Gold-Catalyzed Synthesis of Two Types of Cyclic Ethers 2a and 3a



1a 2a 38% 4a 3a 37%

The formation of **3a** from **1a**[11,12] prompted us to examine the reaction in the presence of π-philic (soft) gold(I) catalysts (Table 3). The desired product **3a** was not formed at all from **1a** in the

Table 3. Optimization of Reaction Conditions in Gold(I)-Catalyzed Synthesis of Cyclic Ethers 3a Having a Carbonyl Group



1a 3a

entry	catalyst (mol %)	solvent	time	yield
1	AuCl (10)	CH_2Cl_2	3 days	–
2	Ph_3PAuCl (10)	CH_2Cl_2	3 days	–
3	$Ph_3PAuOCOCF_3$ (5)	toluene	3 days	–
4	$[Ph_3PAuNTf_2]_2PhMe$ (1)	toluene	18 h	36%
5	$[Ph_3PAuNTf_2]_2PhMe$ (1), 1 equiv of MeOH	toluene	18 h	78%

presence of 10 mol % of AuCl, Ph_3PAuCl, or 5 mol % of $Ph_3PAuOCOCF_3$[14] (entries 1–3), but the reaction using a cationic gold(I) catalyst, $[Ph_3PAuNTf_2]_2PhMe$ (1 mol %), gave cyclic ether **3a** bearing a carbonyl group in 36% yield (entry 4). Further optimization of the reaction conditions using $[Ph_3PAuNTf_2]_2PhMe$ was carried out. As a result, MeOH was found to be efficient as an additive. Thus, treatment of propargylic alcohol **1a** with 1 mol % of $[Ph_3PAuNTf_2]_2PhMe$ and 1 equiv of MeOH[9b,c] smoothly gave cyclic ether **3a** in 78% yield (entry 5).

Next, we examined the scope of the π-philic gold(I)-catalyzed reaction of **1** leading to carbonyl-containing cyclic ethers **3**

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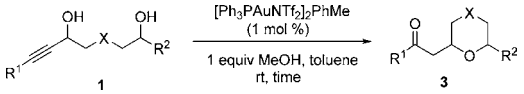
(Table 4). Treatment of alcohols **1** having various substituents at the alkyne terminal with 1 mol % of $[Ph_3PAuNTf_2]_2PhMe$ and 1

Table 4. Gold(I)-Catalyzed Meyer–Schuster Rearrangement Followed by Oxa-Michael Addition

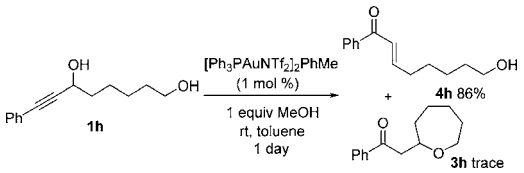


entry	1	R^1	R^2	X	time	yield (*cis*/*trans*)
1	**1i**	*p*-MeO-C_6H_4	H	CH_2	18 h	**3i** 94%
2	**1c**	*n*-Hex	H	CH_2	4 h	**3c** 89%
3	**1d**	*c*-Hex	H	CH_2	1 day	**3d** 82%
4	**1b**	*t*-Bu	H	CH_2	2 days	**3b** 55%
5	**1j** (10:1)	Ph	Me	CH_2	1 day	**3j** 84% (98:2)
6	**1k**	Ph	H	O	20 h	**3k** 89%
7	**1l**	Ph	H	NBoc	1 day	**3l** 67%

equiv of MeOH in toluene at room temperature afforded the corresponding carbonyl-containing cyclic ethers **3** in excellent yield (entries 1–3), except in the case of propargylic alcohol **1b** with a *t*-Bu group, which required a prolonged reaction time and gave only a moderate yield of **3b** (entry 4). A 10:1 diastereomeric mixture of secondary alcohol **1j** also underwent cyclization *cis*-selectively, giving rise to 2,6-tetrahydropyran **3j** in 84% yield (entry 5). The incorporation of oxygen (**1k**) or nitrogen (**1l**) into the ether provided 1,4-dioxane **3k** or morpholine **3l** in 89% and 67% yields, respectively (entries 6 and 7).

Next, we attempted to construct seven-membered ring **3h** under similar reaction conditions, but the reaction with propargylic alcohol **1h** mainly afforded α,β-unsaturated ketone **4h** (86%) with only a trace amount of the desired product **3h** (Scheme 2). To accelerate the oxa-Michael addition of α,β-

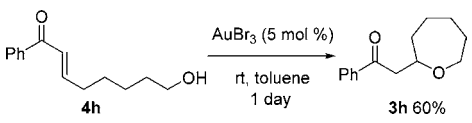
Scheme 2. Attempt to Construct Seven-Membered Ring 3h by Gold(I) Catalyst



unsaturated ketone **4h** produced by Meyer–Schuster rearrangement, we chose an oxophilic (hard) gold(III) catalyst which could activate the carbonyl group by coordination to oxygen.[2,8] Thus, use of the oxophilic gold(III) catalyst $AuBr_3$ (5 mol %) resulted in smooth oxa-Michael addition from α,β-unsaturated ketone **4h**, affording the desired cyclic ether **3h** in good yield (Scheme 3).[15]

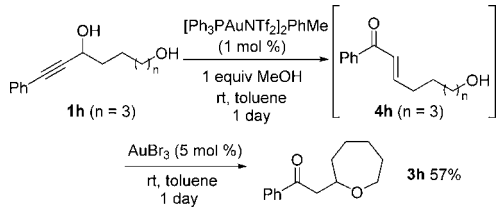
With these results in hand, we tried one-pot synthesis of seven-membered ring **3h** from propargylic alcohol **1h** using a gold(I)

Scheme 3. Acceleration of Oxa-Michael Addition by Oxophilic Gold(III) Catalyst to Construct Seven-Membered Ring 3h



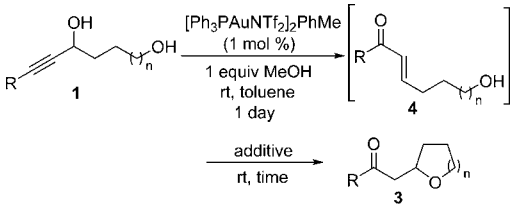
and gold(III) catalyst. After confirming consumption of the starting alcohol **1h** and production of α,β-unsaturated ketone **4h** through gold(I)-catalyzed Meyer–Schuster rearrangement, a gold(III) catalyst (5 mol % of $AuBr_3$) was added to induce oxa-Michael addition, and the desired product **3h** was obtained in good yield (Scheme 4).

Scheme 4. One-Pot Synthesis of Seven-Membered Ring 3h



Next, we examined Meyer–Schuster rearrangement and oxa-Michael addition of other propargylic alcohols **1g,m,n** (Table 5).

Table 5. One-Pot Synthesis of Five- and Seven-Membered Ring 3 by Gold(I)/(III) Catalyst



entry	1	R	*n*	additive (mol %)	time	3 yield
1	**1g**	Ph	1	none	1 day	**3g** 28%
2	**1g**	Ph	1	$AuBr_3$ (5)	1 day	**3g** 83%
3	**1m**	*n*-Hex	1	none	1 day	**3m** 34%
4	**1m**	*n*-Hex	1	$AuBr_3$ (5)	5 h	**3m** 71%
5	**1n**	*n*-Hex	3	none	1 day	**3n** trace
6	**1n**	*n*-Hex	3	$AuBr_3$ (5)	1 day	**3n** 40%

Compounds **1g,m,n** were transformed into cyclic ethers **3g,m,n** in low yields (entries 1 and 3) or in a trace amount (entry 5) in the absence of gold(III) catalyst, whereas the addition of the gold(III) catalyst greatly improved the yields of the products (entries 2, 4, 6). Although a few similar ether formation reactions using noble metal catalysts have been reported,[11,12] their scopes are quite limited. It should be noted that the present method is the first system that provides access to five- to seven-membered cyclic ethers from propargylic alcohols.

A plausible mechanistic model for gold-catalyzed formation of the two types of cyclic ether is shown in Scheme 5. In both cases, the complex **A**[3] would be formed as a common reaction intermediate, whose character would play a pivotal role in determining the reaction pathway. Oxophilic gold(III) in complex **A** strongly activates the hydroxyl group (activation a) to induce cyclization by intramolecular nucleophilic substitution, furnishing cyclic ether **2** bearing an acetylenic moiety. On the other hand, a π-philic gold(I) catalyst strongly activates the triple bond of propargylic alcohols **1** (activation b). Thus, activation b by π-philic gold(I) promotes addition of methanol[9c] (**A** → **B**) to generate an allenyl ether (**B** → **C** → **D**), which undergoes hydrolysis (**D** → **E**) to afford α,β-unsaturated ketone **E**. In the case of six-membered ring formation, ketone **E** ($n = 2$) cyclizes smoothly to give **3** ($n = 2$) because it has the lowest ring strain. In the case of five- or seven-membered ring formation ($n = 1$ or 3),

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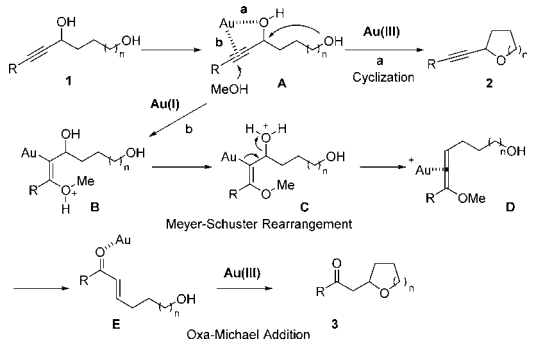
Scheme 5. Mechanistic Proposal for Gold(III)-Catalyzed Cyclization and Gold(I)-Catalyzed Meyer−Schuster Rearrangement Followed by Gold(III)-Catalyzed Oxa-Michael Addition



oxophilic (hard) gold(III) activates the carbonyl group of **E** (n = 1 or 3) efficiently[8] to furnish cyclic ethers **3** (n = 1 or 3) having a carbonyl group.

In summary, we present gold(I)/(III)-catalyzed regiodivergent syntheses of two types of cyclic ethers from propargylic alcohols, by making use of the hard−soft principle. We are currently applying the method to the synthesis of biologically active cyclic ether derivatives. Experimental and theoretical investigations on the reaction mechanism are also in progress.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data, ^{1}H and ^{13}C NMR spectra, and HRMS for all novel compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01046.

■ AUTHOR INFORMATION

Corresponding Authors

* E-mail: morita@ac.shoyaku.ac.jp.
* E-mail: tamura@ac.shoyaku.ac.jp.

Notes

The authors declare no competing financial interest.

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