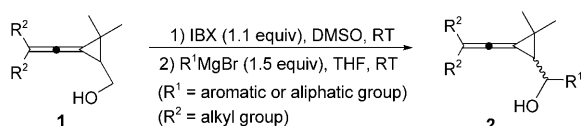


Gold(I) and Brønsted Acid Catalyzed Intramolecular Rearrangements of Vinylidenecyclopropanes

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Vinylidenecyclopropanes (VDCPs) are highly strained but thermally stable and adequately reactive substances that serve as extremely versatile building blocks in many organic reactions. Over the last few decades, due to their unique structural and electronic properties, the chemistry of VDCPs has attracted much attention from mechanistic, spectroscopic, and synthetic viewpoints and a wide variety of transformations have been disclosed.^[1,2] For example, numerous ring-opening/cycloaddition and intramolecular rearrangement reactions of VDCPs catalyzed or mediated by transition metals or Lewis and Brønsted acids have been disclosed extensively thus far.^[3,4] Meanwhile, gold catalysts, because of their unique properties of activating alkynes, alkenes, and alkenes toward attack from a variety of nucleophiles, have now become a well-established choice for many chemical transformations.^[5] Recently, we synthesized a series of vinylidenecyclopropanes **2**^[6] containing an additional secondary alcohol chain on the cyclopropanes from vinylidenecyclopropanes **1** (Scheme 1, for a detailed description,



Scheme 1. Synthesis of VDCPs **2** containing a secondary alcohol chain; IBX = 2-iodoxybenzoic acid.

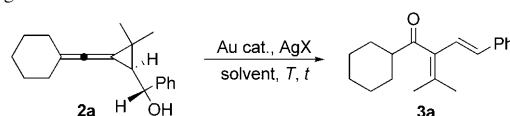
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Supporting information for this article, including experimental procedures, compound characterization data, and X-ray crystal data of **3a** is available on the WWW under <http://dx.doi.org/10.1002/chem.201001433>.

see the Supporting Information). To our delight, we found that in the presence of gold(I) or a Brønsted acid, VDCPs **2** could undergo different intramolecular rearrangements to give, respectively, enone or enyne derivatives in moderate to good yields under mild conditions. To the best of our knowledge, this is the first example of a gold(I)-catalyzed intramolecular rearrangement of VDCPs containing a secondary alcohol chain. Herein, we wish to report the results of these interesting reactions.

Initially, the reactions were carried out by using VDCP **2a** (only one diastereoisomer with *anti*-configuration as determined by a NOESY spectrum) as the substrate in the presence of a gold(I) catalyst and the results are summarized in Table 1. We found that (*E*)-1-cyclohexyl-3-methyl-2-styrylbut-2-en-1-one (**3a**) was obtained stereospecifically as a single stereoisomer in 63 % yield in THF at room temperature in the presence of Ph₃PAuCl (10 mol %) and AgOTf (10 mol %; OTf = trifluoromethanesulfonate) (Table 1,

Table 1. Optimization of the reaction conditions for the gold(I)-catalyzed rearrangement of VDCP **2a**.



Entry ^[a]	Solvent	Au cat.	AgX	T [°C]	t [h]	Yield [%] ^[b]
1	THF	PPh ₃ AuCl	AgOTf	RT	20	63
2	CH ₂ Cl ₂	PPh ₃ AuCl	AgOTf	RT	20	33
3	DCE	PPh ₃ AuCl	AgOTf	RT	20	trace
4	MeCN	PPh ₃ AuCl	AgOTf	RT	20	37
5	toluene	PPh ₃ AuCl	AgOTf	RT	20	89
6	MeOH	PPh ₃ AuCl	AgOTf	RT	20	78
7	toluene	–	AgOTf	RT	24	– ^[c]
8	toluene	PPh ₃ AuCl	–	RT	20	22 ^[d]
9	toluene	PPh ₃ AuCl	AgBF ₄	RT	20	85
10	toluene	PPh ₃ AuCl	AgSbF ₆	RT	20	26
11	toluene	PPh ₃ AuCl	AgOTf	40	6	89

[a] All reactions were carried out using **2a** (0.1 mmol) in the presence of catalyst (10 mol %) in various solvents (1.0 mL). [b] Yield of the isolated product. [c] Product **4a** was obtained in 40 % yield and **5a** was formed in 31 % yield. [d] 63 % of **2a** was recovered. DCE = 1,2-dichloroethane.

entry 1). The crystal structure of **3a** was unambiguously determined by X-ray diffraction (Figure 1) and its CIF data are presented in the Supporting Information.^[7] Screening of

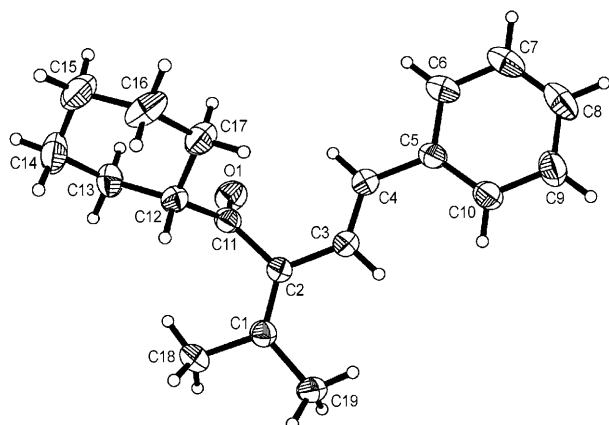
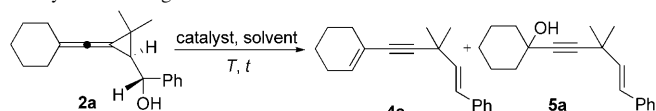


Figure 1. ORTEP drawing of **3a** ellipsoids at 30% probability.

the solvents revealed that toluene was the optimal solvent, affording **3a** in 89% yield (Table 1, entries 2–6). Furthermore, we found that using AgOTf alone as the catalyst in toluene at room temperature afforded enyne derivative **4a** and alcohol derivative **5a** (see Table 2) in 40% and 31% yield, respectively, instead of **3a** (Table 1, entry 7). When using PPh₃AuCl alone as the catalyst, compound **3a** was obtained in 22% yield along with 63% of recovered substrate, suggesting that the in situ generated gold(I) species is the efficient catalyst (Table 1, entry 8). Another silver salt, namely AgBF₄ also produced **3a** in an excellent yield as a single stereoisomer (Table 1, entry 9). The combination of AuPPh₃Cl/AgSbF₆ did not have efficient catalytic activity in this reaction (Table 1, entry 10). Increasing the reaction temperature to 40 °C resulted in the same yield as that obtained at room temperature with a shorter reaction time (Table 1, entry 11). Therefore, the best reaction conditions have been identified as a combination of AuPPh₃/AgOTf as the catalyst in toluene at 40 °C (Table 1, entry 11).

On the other hand, VDCP **2a** could undergo a totally different intramolecular rearrangement in toluene at room temperature in the presence of trifluoromethanesulfonic acid (TfOH, 10 mol%). The enyne derivative **4a** was produced in 49% yield along with the alcohol derivative **5a** in 33% yield (Table 2, entry 1). Using THF or MeOH as the solvent, the products **4a** and **5a** were obtained in good total yields (Table 2, entries 2 and 3). In dichloromethane, complex product mixtures were formed under identical conditions (Table 2, entry 4). Interestingly, in MeCN, **4a** was formed in 82% yield as the sole product, suggesting that the effects of the solvent significantly affected the reaction outcome (Table 2, entry 5). Other Brønsted acids, such as MeSO₃H and CF₃CO₂H are not as effective as HOTf under the similar conditions (Table 2, entries 6 and 7). Thus, the best conditions for the formation of the corresponding enyne derivative **4a** were found to be those in MeCN at

Table 2. Optimization of the reaction conditions for the Brønsted acid catalyzed rearrangement of VDCP **2a**.



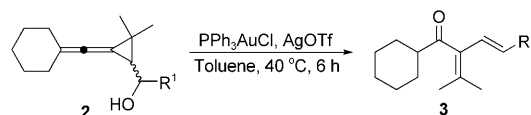
Entry ^[a]	Solvent	Catalyst	T [°C]	t [h]	Yield [%] ^[b]	
					4a	5a
1	toluene	HOTf	RT	3	49	33
2	THF	HOTf	RT	3	53	33
3	MeOH	HOTf	RT	3	44	26
4	CH ₂ Cl ₂	HOTf	RT	3	complex mixture	
5	MeCN	HOTf	RT	3	82	–
6	MeCN	MeSO ₃ H	RT	3	41	26
7	MeCN	CF ₃ CO ₂ H	60	12	23	52

[a] All reactions were carried out using **2a** (0.1 mmol) in the presence of catalyst (10 mol%) in various solvents (1.0 mL). [b] Yield of the isolated product.

room temperature with 10 mol% of HOTf (Table 2, entry 5).

Having optimized the reaction conditions, we next examined the generality of these interesting intramolecular rearrangement reactions of VDCPs **2** (in which R², R² = –(CH₂)₅– and R¹ = aromatic or aliphatic group) in the presence of gold(I) or a Brønsted acid and the results were summarized in Tables 3 and 4, respectively. VDCPs **2b–2e** and **2g–2h** containing an electron-withdrawing or electron-do-

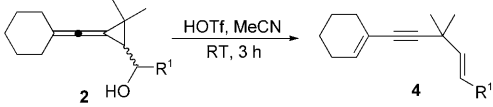
Table 3. Gold(I)-catalyzed rearrangement of VDCPs **2** under the optimal conditions.



Entry ^[a]	2 , R ¹ , (d.r.)	Yield [%] ^[b]
1	2b , <i>p</i> -BrC ₆ H ₄ , (7.1:1.0)	3b , 87
2	2c , <i>p</i> -MeC ₆ H ₄ , – ^[c]	3c , 84
3	2d , <i>p</i> -MeOC ₆ H ₄ , – ^[c]	3d , 83
4	2e , <i>p</i> -C ₆ H ₅ C ₆ H ₄ , – ^[c]	3e , 85
5	2f , β-C ₁₀ H ₇ , – ^[c]	3f , 75
6	2g , <i>m</i> -ClC ₆ H ₄ , – ^[c]	3g , 76
7	2h , 3,5-Me ₂ C ₆ H ₃ , – ^[c]	3h , 77
8	2i , <i>o</i> -MeC ₆ H ₄ , – ^[c]	complex mixture
9	2j , Et (1.1:1.0)	complex mixture
10	2k , CH ₂ C ₆ H ₁₁ , – ^[c]	complex mixture
11	2l , CH ₂ C ₆ H ₅ , – ^[c]	complex mixture

[a] All reactions were carried out using **2** (0.1 mmol) in the presence of PPh₃AuCl/AgOTf (10 mol%) in toluene (1.0 mL) at 40 °C. [b] Yield of the isolated product. [c] Only one diastereoisomer was isolated.

nating group at the *para*- or *meta*-position of the phenyl ring produced the corresponding products **3** in 76 to 87% yields under the optimized conditions of the gold(I)-catalyzed reaction (Table 3, entries 1–4, 6, and 7). In addition, for VDCP **2f** in which R¹ = 2-naphthyl, the reaction also proceeded smoothly to give **3f** in 75% yield (Table 3, entry 5). However, when there was a methyl group at the *ortho*-posi-

Table 4. Brønsted acid catalyzed rearrangement of VDCPs **2** under the optimal conditions.


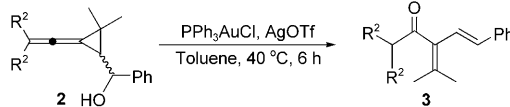
Entry ^[a]	2 , R ¹ , (d.r.)	Yield [%] ^[b]
1	2b	4b , 80
2	2c	4c , 81
3	2d	4d , 75
4	2e	4e , 76
5	2f	4f , 67
6	2h	4h , 76
7	2i	4i , 72
8	2j , Et (1.1:1.0)	4j , 45
9	2k , CH ₂ C ₆ H ₁₁ , ^{−[c]}	4k , 55
10	2l , CH ₂ C ₆ H ₅ , ^{−[c]}	4l , 53

[a] All reactions were carried out using **2** (0.1 mmol) in the presence of HOTf (10 mol %) in MeCN (1.0 mL) at RT. [b] Yield of the isolated product. [c] Only one diastereoisomer was isolated.

tion of the benzene ring, the expected rearrangement product could not be obtained, presumably due to the steric hindrance of the aromatic ring (Table 3, entry 8). For the VDCPs **2j–2l** (R¹=aliphatic group), complex product mixtures were formed under identical conditions without formation of the desired products, presumably due to the fact that the corresponding cationic intermediates could not be stabilized by the aliphatic group in these substrates.

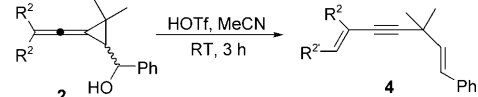
In the case of the Brønsted acid catalyzed reaction, VDCPs **2b–2e** and **2h** with electron-withdrawing or electron-donating groups at the *para*- or *meta*-position of the phenyl ring produced the enyne derivatives **4b–4e** and **4g** in 75–81 % yields under the standard conditions (Table 4, entries 1–4 and 6). Even for VDCP **2i** in which R¹=*o*-MeC₆H₄, the rearrangement reaction could also proceed smoothly to give **4h** in 72 % yield (Table 4, entry 7). In the case of VDCP **2f**, the product **4f** was afforded in 67 % yield (Table 4, entry 5). Furthermore, we found that this reaction was also suitable for the substrates **2j–2l** with aliphatic substituents, producing enyne derivatives **4i–4k** in moderate yields, (Table 4, entries 8–10).

To extend the scope of these two reactions, other VDCPs **2m–2q** (R¹=phenyl group, R²=aliphatic group) were also examined under the standard conditions and the results of these experiments are summarized in Tables 5 and 6. It was found that by either expanding the six-membered ring to a seven-membered ring or contracting it to a five-membered ring, the gold(I)-catalyzed reactions could still proceed smoothly to give **3j** and **3l** in 74 and 88 % yield, respectively (Table 5, entries 2 and 4). The substrate **2o** containing a cyclohexyl group with three methyl substituents afforded the product **3k** in 88 % yield (Table 5, entry 3). As for the substrate **2m** (R²=butyl), the product **3i** was obtained in 84 % yield (Table 5, entry 1). The substrate **2q** with a methyl substituent also gave the corresponding enone derivative **3m** in 80 % yield (Table 5, entry 5).

Table 5. Gold(I)-catalyzed rearrangement of VDCPs **2** under the optimized conditions.


Entry ^[a]	2 , R ² , R ² , (d.r.)	Yield [%] ^[b]
1	2m , Bu, Bu, ^{−[c]}	3i , 84
2	2n , ^{−(CH₂)₆−} , ^{−[c]}	3j , 74
3	2o , (several diastereomeric mixtures)	3k , 88
4	2p , ^{−(CH₂)₄−} , ^{−[c]}	3l , 88
5	2q , Me, Me, ^{−[c]}	3m , 80

[a] All reactions were carried out using **2** (0.1 mmol) in the presence of PPh₃AuCl/AgOTf (10 mol %) in toluene (1.0 mL) at 40 °C. [b] Yield of the isolated product. [c] Only one diastereoisomer was isolated.

Table 6. Brønsted acid catalyzed rearrangement of VDCPs **2** under the optimal conditions.


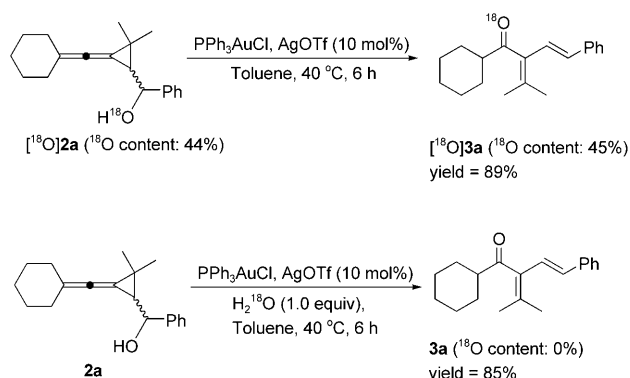
Entry ^[a]	2	Yield [%] ^[b]
1	2m	4l , 82 ^[c]
2	2n	4m , 80
3	2o	4n , 77 ^[d]
4	2p	4o , 81
5	2q	4p , 79 (R ² =H)

[a] All reactions were carried out using **2** (0.1 mmol) in the presence of HOTf (10 mol %) in MeCN (1.0 mL) at RT. [b] Yield of the isolated product. [c] The corresponding enyne was obtained with *trans*-configuration. [d] Diastereomeric mixtures with 1.1:1.0 ratio.

Moreover, when the Brønsted acid catalyzed reaction was carried out using VDCPs **2n**, **2p** (R², R²=cyclic substituents) or **2m**, **2q** (R², R²=non-cyclic substituents) as the substrates, it was found that the corresponding rearranged products were produced in 79–82 % yields under the standard conditions (Table 6, entries 1, 2, 4, and 5). It should be noted that using VDCP **2o** (several diastereoisomeric mixtures) as the substrate led to the enyne derivative **4n** as a diastereoisomeric mixture in a good combined yield with a 1.1:1.0 ratio (Table 6, entry 3).

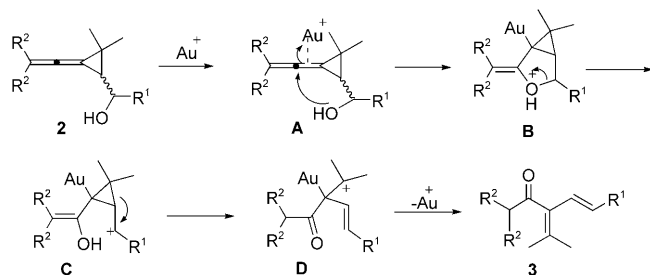
To clarify the reaction mechanism of the gold(I)-catalyzed intramolecular rearrangement, an isotopic labeling experiment was conducted wherein the ¹⁸O-enriched secondary alcohol [¹⁸O]**2a** (¹⁸O content 44 %) was synthesized and used in the gold(I)-catalyzed reaction under the standard conditions.^[8] It was found that the corresponding product [¹⁸O]**3a** was obtained in 89 % yield with an ¹⁸O content of 45 %. Using **2a** as the substrate with the addition of 1.0 equiv of H₂¹⁸O in the reaction system, it was found that enone derivative **3a** was formed in 85 % yield with an ¹⁸O content of

0%, indicating that the oxygen atom of the product **3a** is indeed derived from substrate **2a** and therefore the intramolecular cyclization is responsible for the formation of **3a** (Scheme 2).

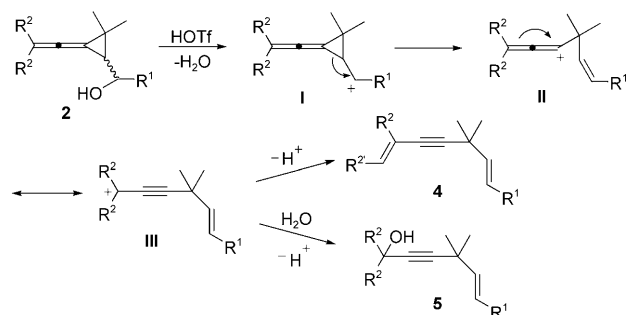


Scheme 2. Isotopic labeling experiment using $[^{18}\text{O}]\mathbf{2a}$ as the substrate and adding H_2^{18}O into the reaction under the standard conditions.

Plausible mechanisms for the formation of the enone and enyne derivatives are outlined in Scheme 3 and Scheme 4, respectively. In the gold(I)-catalyzed reaction, the allene functionality of **2** is activated by gold(I) to form intermediate **A**. The intramolecular nucleophilic addition by the hydroxyl group onto the electrophilic carbon center in intermediate **A**^[9] gives intermediate **B**,^[10] which undergoes a cation-induced rearrangement to produce intermediate **C**. Subsequent ring-opening of the cyclopropane forms Au-con-



Scheme 3. A plausible mechanism for the formation of **3**.



Scheme 4. A plausible mechanism for the formation of **4** and **5**.

taining intermediate **D**, which affords the final product **3** through the elimination of gold(I).

In Scheme 4, in the presence of the Brønsted acid HOTf, VDCP **2** is first protonated by TfOH at the hydroxyl group along with the liberation of one molecule of water to give a stabilized cationic intermediate **I**, which undergoes cyclopropane ring opening to afford the corresponding intermediate **II** and a resonance-stabilized intermediate **III**. Intermediate **III** provides product **4** by deprotonation or through attack by water to give the product **5**.

In conclusion, we have developed two distinct gold(I) and Brønsted acid catalyzed intramolecular rearrangements of VDCPs **2** containing a secondary alcohol chain to produce enone and enyne derivatives in moderate or good yields under mild conditions. The scope and limitations of the two reactions have been carefully examined and the reaction mechanisms have been discussed on the basis of ^{18}O -isotope labeling experiments. The rearrangement products **3** and **4** are important building blocks in organic chemistry. The potential utilization and extension of the scope of this synthetic methodology are currently under investigation.

Experimental Section

General procedure for the gold-catalyzed rearrangement: Under an argon atmosphere, vinylidenecyclopropane **2a** (0.1 mmol), AuPPh_3Cl (0.01 mmol), AgOTf (0.01 mmol), and toluene (1 mL) were added to a Schlenk tube. The reaction mixture was stirred at 40 °C for 6 h and the reaction was monitored by TLC. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (silica gel; eluent: EtOAc/petroleum ether (PE)=1:20). Compound **3a** was isolated as a yellow oil in 89 % yield.

General procedure for the Brønsted acid catalyzed rearrangement: Under an argon atmosphere, vinylidenecyclopropane **2a** (0.1 mmol), HOTf (0.01 mmol), and MeCN (1 mL) were added to a Schlenk tube. The reaction mixture was stirred at RT until the reaction was complete. Then, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel; eluent: EtOAc/PE=1:50). Compound **4a** was isolated as a yellow oil in 82 % yield.

Acknowledgements

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Keywords: Brønsted acid • cyclopropanes • gold • reaction mechanisms • rearrangement

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