Novel Carbon—Carbon Bond Formation from Propargylic Alcohols and Olefin toward Five-Membered Heterocyclic Rings Catalyzed by AgSbF₆

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ABSTRACT



A mild and direct process for C-C bond formation from propargylic alcohols and olefin has been developed in the presence of a silver catalyst. In this reaction, trace amounts of water were necessary and allene alcohols 2 and 1,3-dienes 3 were obtained selectively.

The development of novel methods for the annulation of fivemembered heterocyclic rings is very important in the field of synthetic organic chemistry because such heterocyclic compounds are useful synthetic intermediates as well as important structural units found in natural and artificial products.¹ For example, kainic acid and allokainic acid, isolated from marine alga, attract the interest of synthetic chemists.²

Recently, transition-metal-catalyzed cyclization reactions of carbon-hetero formation (via *path a*) and carbon–carbon formation (via *path b*) represent an effective and straightforward methodology for the synthesis of this heterocyclic compounds (Scheme 1).³

Silver "catalysts", as a transition metal catalyst, are commonly considered to have low efficiency and not to be



as good as other late transition metals. On the other hand, silver(I) complexes are generally used as stoichiometric oxidants for the oxidation of various organic or inorganic substrates. Many reports used silver(I) complexes as catalysts

^{(1) (}a) Porter, A. E. A. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 3, pp 157–197. (b) Sainsburg, M. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 3, pp 995–1038. (c) Sharp, J. T. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 7, pp 593–651.

⁽²⁾ Takano, S.; Sugihara, T.; Satoh, S.; Ogasawara, K. J. Am. Chem. Soc. 1988, 110, 6467, and references therein.

⁽³⁾ For recent reviews, see: (a) Patil, N. T.; Yamamoto, Y. Chem. Rev. 2008, 108, 3395. (b) Nakamura, I.; Yamamoto, Y. Chem. Rev. 2004, 104, 2127. (c) McReynolds, M. D.; Dougherty, J. M.; Hanson, P. R. Chem. Rev. 2004, 104, 2239. (d) Alonso, F.; Beletskaya, I. P.; Yus, M. Chem. Rev. 2004, 104, 3079. (e) Deiters, A.; Martin, S. F. Chem. Rev. 2004, 104, 2019. (f) Zeni, G.; Larock, R. C. Chem. Rev. 2004, 104, 2285. (g) Yet, L. Chem. Rev. 2000, 100, 2963. (h) Tsuji, J. Transition Metal Reagents and Catalysts; John Wiley & Sons Ltd.: New York, 2000. (i) Transition Metals for Organic Synthesis; Beller, M., Bolm, C., Eds.; Wiley-VCH Verlag GmbH: Weinheim, 1998. (j) Transition Metal Catalyzed Reactions; Murahashi, S., Davies, S. G., Eds.; Blackwell Science: Oxford, 1999.

in oxidation or group-transfer reactions,⁴ although recent studies have shown that silver species exhibited interesting catalytic activities functioning for carbon-hetero formation.^{5,6} However, examples of the carbocyclization catalyzed by silver are limited.⁷ In the context of our ongoing efforts to develop tandem reactions, we anticipated that a new domino process initiated by silver induced C–C bond formation followed by subsequent trace amounts of water attack (Scheme 2) might be achieved. Herein, we reported a novel



carbon-carbon bond formation from propargylic alcohols and olefin toward five-membered heterocyclic rings in the presence of $AgSbF_6$. In this reaction, trace amounts of water were necessary and olefin as the intramolecular nucleophilic with propargylic alcohols were selectively transformed into allene alcohols and 1,3-dienes.

Initially, we started by using 0.3 mmol of N-(4-hydroxy-4-phenylbut-2-ynyl)-N-(3-methylbut-2-enyl)-toluenesulfona-

 Table 1. Transition-Metal Catalysts for the Transformation of 1a to 2a

	TsNOH Ph 1a	M solvent	sN 2a	∠OH ∕∕Ph	
			temp	time	yield
entry	catalyst (mol %)	solvent	(°C)	(h)	(%) ^a
1	$AgSbF_{6}(5)$	$\mathrm{CH}_2\mathrm{Cl}_2$	\mathbf{rt}	20	80
2	$AgSbF_{6}\left(10 ight)$	$\mathrm{CH}_2\mathrm{Cl}_2$	\mathbf{rt}	15	88
3	$AgSbF_{6}(15)$	$\rm CH_2 \rm Cl_2$	\mathbf{rt}	12	87
4	$AgSbF_{6}\left(10 ight)$	$\rm CH_2 \rm Cl_2$	15	20	92
5	$AgSbF_{6}\left(10 ight)$	$\rm CH_2 \rm Cl_2$	0	24	80
6	$AgSbF_{6}\left(10 ight)$	dry CH ₂ Cl ₂	15	24	с
7	AgOTf (10)	$\rm CH_2 \rm Cl_2$	15	24	0
8	$AgBF_4(10)$	$\rm CH_2 \rm Cl_2$	15	24	0
9	$AgNTf_{2}(10)$	$\rm CH_2 \rm Cl_2$	15	24	73
10^b	$AgOOCCF_3(10)$	$\mathrm{CH}_{2}\mathrm{Cl}_{2}$	15	24	0
11	$AlCl_3(10)$	$\mathrm{CH}_2\mathrm{Cl}_2$	15	24	0
12	$FeCl_3(10)$	$\mathrm{CH}_{2}\mathrm{Cl}_{2}$	15	24	c
13	TsOH (10)	CH_2Cl_2	15	24	13
14	$F_3CCOOH(10)$	$\mathrm{CH}_{2}\mathrm{Cl}_{2}$	15	24	c
15^b	TfOH(10)	$\mathrm{CH}_{2}\mathrm{Cl}_{2}$	15	24	d
16	$AgSbF_{6}\left(10 ight)$	$ClCH_2CH_2Cl$	15	18	91
17	$AgSbF_{6}\left(10 ight)$	THF	15	24	0
18	$AgSbF_{6}\left(10 ight)$	$CH_{3}OH$	15	24	0
19	$AgSbF_{6}\left(10 ight)$	toluene	15	24	0
20	$AgSbF_{6}\left(10\right)$	$\mathrm{CH}_3\mathrm{NO}_2$	15	24	0
	1	,			

 a Isolated yield. b Decomposed. c Trace. d For details, see Supporting Information.

Table 2. AgSbF₆-Catalyzed Synthesis of Allene Alcohols 2from Propargylic Alcohols 1^a





 a Conditions: 0.3 mmol of 1 with 10 mol % of catalyst in CH₂Cl₂ (2.0 mL) at 15 °C. b Isolated yield.

mide 1a and 5 mol % of AgSbF₆ in wet CH₂Cl₂ at room temperature; to our delight, the desired product 2-(4-(2phenylvinylidene)-1-tosylpyrrolidin-3-yl)propan-2-ol 2a was formed in 80% yield after 20 h. On increasing the amount of catalyst to 10 mol %, a 88% yield of 2a was obtained after 15 h, when the silver salt was added to 15 mol %, but no higher yield was obtained (Table 1, entries 1-3). Then we decrease temperature to 15 °C, an excellent yield of 2awas obtained with 10 mol % AgSbF₆ (up to 92%) (Table 1, entry 4). The reaction was also tested in dry CH₂Cl₂ at 15 °C; only trace amounts of 2a was observed (Table 1, entry 6). Other silver catalysts, such as AgOTf, AgBF₄, AgNTf₂, AgOOCCF₃ gave no better results (Table 1, entries 7-10). AlCl₃ and FeCl₃, including protic acids such as TsOH, TFA and TfOH have also been applied to the reaction, no superior results were obtained (Table 1, entries 11-15). Other solvents were also tested in the reaction, only DCE gave good yield. Thus, the use of $AgSbF_6$ (10 mol %) in wet CH₂Cl₂ at 15 °C was found to be the most efficient and used as the standard conditions.

With the optimized conditions in hand, various representative propargylic alcohols **1a**–**1** were then submitted to the

Table 3. AgSbF₆-Catalyzed Synthesis of 1,3-dienes 3 from Propargylic Alcohols 1^a



^a Conditions: 0.3 mmol of 1 with 10 mol % of catalyst in CH₂Cl₂ (2.0 mL) at 15 °C. ^b Isolated yield. ^c The reaction was carried out at 40 °C.

above conditions, as depicted in Table 2. Thus, a tandem carbon-carbon and carbon-oxygen bond formation of propargylic alcohols 1a-f and 1h-k proceeded smoothly to provide corresponding products 2a-f and 2h-k in moderate to excellent yields. The reaction works well with aromatic R¹ groups. Electron-withdrawing aryl groups showed better results than those with an electron-rich group in this tandem reaction (1b vs 1c). Substrate 1d with a heteroaromatic R¹ group can also afford the desired product 2d in 73% yield, while a substrate like 1g with an aliphatic R¹ group gave no reaction. Other substrates like 1h-k can also afford corresponding furan derivatives 2h-k in moderate yield. Interestingly, substrate like 1l with steric effects gave no reaction.

Furthermore, to expand the scope of this reaction, we also investigated a range of propargylic alcohols; it was found that under the silver catalyst some substrates 1 transferred into 1,3-dienes 3 directly, without giving the products 2 as depicted in Table 3. Various representative propargylic alcohols 1m-u transferred into corresponding products 3m-u in moderate to excellent yields (up to 97%) (Figure 1).



Figure 1. X-ray structure of 3q.⁸

To uncover the mechanism for the reaction, we started out by using propargylic alcohol **1m** under the standard conditions, and the desired product **2m** was isolated in 30%

⁽⁴⁾ For selected papers, see: (a) Li, Z.; Capretto, D. A.; Rahaman, R.;
He, C. Angew. Chem., Int. Ed. 2007, 46, 5184. (b) Cui, Y.; He, C. Angew.
Chem., Int. Ed. 2004, 43, 4210. (c) Clark, T. B.; Woerpel, K. A. J. Am.
Chem. Soc. 2004, 126, 9522. (d) Cui, Y.; He, C. J. Am. Chem. Soc. 2003, 125, 16202. (e) Josephsohn, N. S.; Snapper, M. L.; Hoveyda, A. H. J. Am.
Chem. Soc. 2003, 125, 4018. (f) Momiyama, N.; Yamamoto, H. J. Am.
Chem. Soc. 2003, 125, 6038. (g) Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J. J. Am. Chem. Soc. 2003, 125, 9270.

⁽⁵⁾ For selected recent examples of Ag-catalyzed reviews, see: (a) Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3199. (b) Weibel, J.-M.; Blanc, A.; Pale, P. *Chem. Rev.* **2008**, *108*, 3149. (c) Álvarez-Corral, M.; Muñoz-Dorado, M.; Rodríguez-García, I. *Chem. Rev.* **2008**, *108*, 3174. (d) Li, Z.; He, C. *Eur. J. Org. Chem.* **2006**, 4313.

⁽⁶⁾ For selected examples of Ag-catalyzed reactions, see: (a) Umeda,
R.; Studer, A. Org. Lett. 2008, 10, 993. (b) Mandai, H.; Mandai, K.; Snapper,
M. L.; Hoveyda, A. H. J. Am. Chem. Soc. 2008, 130, 17961. (c) Yong,
S. W.; Eom, J. I. J. Org. Chem. 2006, 71, 6705. (d) Yang, C.-G.; Reich,
N. W.; Shi, Z.; He, C. Org. Lett. 2005, 7, 4553. (e) Yao, X.; Li, C.-J. Org.
Lett. 2005, 7, 4395. (f) Patil, N. T.; Pahadi, N. K.; Yamamoto, Y. J. Org.
Chem. 2005, 70, 10096. (g) Wei, C.; Li, Z.; Li, C.-J. Org. Lett. 2003, 5, 4473.

 ^{(7) (}a) Yao, X.; Li, C.-J. J. Org. Chem. 2005, 70, 5752. (b) Harrison,
 T. J.; Dake, G. R. Org. Lett. 2004, 6, 5023. (c) Sweis, R. F.; Schramm,
 M. P.; Kozmin, S. A. J. Am. Chem. Soc. 2004, 126, 7442.

yield after 2 h,⁹ and only a trace amount of **3m** was observed. When the reaction was carried out for 10 h under the above conditions, and only a trace amount of **2m** was observed; also, a 50% yield of **3m** was isolated (Scheme 3).



On the basis of the above observations, we propose the following plausible mechanisms for this cascade transformation (Scheme 4). (i) Coordination of the alkynyl moiety and hydroxy of **A** to $AgSbF_6$ gives the complex **B**. (ii) The subsequent domino trace amounts of water as the nucleophilic attack the olefin and occurs carbocyclization affords intermediate allene alcohol cation **C**. (iii) Intermediate **C** releases the hydrogen cation to afford the allene alcohol **D** and regenerates the catalyst $AgSbF_6$. (iv) Coordination of the allene moiety of **D** to Ag catalyst gives the complex **E**. (v) Some of allene alcohols occur domino carbon–carbon bond cleavage and afford the intermediate **F**. (IV) Protonation of **F** yields 1,3-dienes **G** and regenerates the catalyst Ag. In this reaction, trace amounts of water played an important role.

In summary, a mild and direct process for C-C bond formation from propargylic alcohols and olefin has been developed in the presence of a silver catalyst. In this reaction, trace amounts of water were necessary and propargylic alcohols with olefin were selectively transformed into five-



member heterocyclic compounds allene alcohols 2 and 1,3dienes 3 containing various functionalities. A more detailed investigation on the mechanism, as well as the scope of this cascade, is ongoing in our laboratory.

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Supporting Information Available: Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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⁽⁸⁾ The molecular structure of the corresponding product 1q was determined by means of X-ray crystallographic studies; for details, see the Supporting Information.

⁽⁹⁾ The product 2m may be not stable, and only 30% yield was isolated by flash column chromatography.