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Silver(I)-Catalyzed Dual Activation of Propargylic Alcohol and Aziridine/Azetidine: Triggering Ring-Opening and Endo-Selective Ring-Closing in a Cascade

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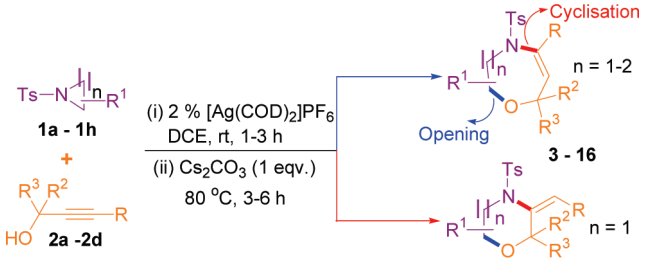

$[Ag(COD)_2]PF_6$ catalyzes the reaction between propargyl alcohols and *N*-tosylaziridines/azetidines leading to a diverse range of *N*,*O*-heterocycles, namely, oxazines, oxazepines, and oxazocines via ring-opening and ring-closing in a cascade

In recent years tandem catalysis has attracted widespread attention from synthetic chemists who aim at constructing complex molecular architecture from simple building blocks.[1] Tandem catalysis involving a transition metal is often distinguished by (i) selective binding of multiple substrates across the active site(s), (ii) making and breaking of multiple bonds in a cascade, and (iii) the presence of more than one distinct catalytic event.[2] Therefore the success in tandem catalysis is interalia dependent on the degree of synchronization of the above events.[3] A major ongoing program in our laboratory is in late transition metal catalysis, where the goal is to realize differential binding, dual-activation, and coupling between a π-system and a substrate having a hard-donor center.[4] During the course of our studies we were attracted by the potential of coinage metals in general, and silver(I) in particular, to bind/activate π-systems such as an arene, alkene, or an alkyne on one hand and substrates bearing a heteroatom such as N, O, and S on the other.[5,6] These features make the coinage metals trustworthy candidates in facilitating three important reactions, namely (i) the opening of a heterocyclic ring by an internal/external nucleophile, (ii) the nucleophilic addition across an alkene/alkyne by an external nucleophile, and (iii) internal nucleophilic attack across an alkene/alkyne leading to a ring closure (Figure 1).[7–9]

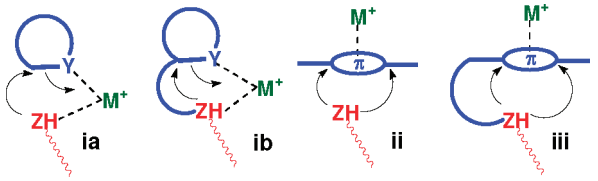

FIGURE 1. Coinage metal (M) assisted binding and ring-opening events.

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(7) Selected examples of heterocycle ring opening by a nucleophile: (a) Sun, X.; Sun, Y.; Fan, R.; Wu, J. *Adv. Synth. Catal.* **2007**, *349*, 2151. (b) Wang, J. Y.; Hu, Y.; Wang, D. X.; Pan, J.; Huang, Z. T.; Wang, M. X. *Chem. Commun.* **2009**, 422. (c) Li, P.; Evans, C. D.; Juollie, M. M. *Org. Lett.* **2005**, *7*, 5325. (d) Rao, R. K.; Naidu, A. B.; Sekar, G. *Org. Lett.* **2009**, *11*, 1923. (e) Hajra, S.; Maji, B.; Mal, D. *Adv. Synth. Catal.* **2009**, *351*, 859.

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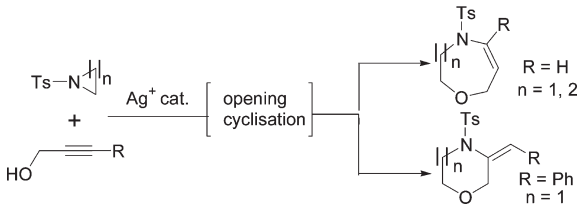
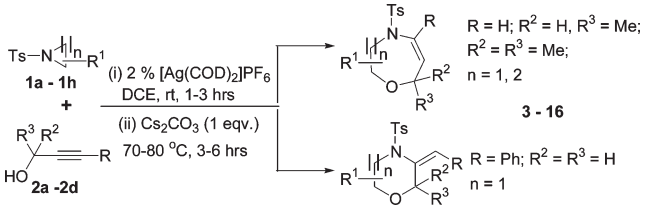
Note that, when stitched in a 2-in-1 or 3-in-1 cascade, the above three reactions can potentially generate myriad opportunities in multicomponent synthesis.[10] Keeping the above in view, we searched the literature on Ag(I)-catalysis where such cascade reactions ultimately resulted in a heterocycle. However, such examples are few.[11] Continuing on our success in propargylic activation[12] and aziridine ring-opening[13] we are delighted to present here a Ag(I)-catalyzed tandem ring-opening and ring-closing involving propargylic alcohol and aziridine or azetidine resulting in the formation of 6-, 7-, and 8-membered *N*,*O*-heterocycles, namely oxazines, oxazepines, and oxazocines.[14] The reaction is characterized by two main catalytic events operating in a cascade. In the first event the aziridine or azetidine ring is opened via nucleophilic attack by propargylic alcohol. In the second event the tethered *N*-nucleophile in the intermediate attacks the alkynic/allenic appendage leading to 100% endoselective ring-closing (Scheme 1).

SCHEME 1



The model reaction between cyclohexyl-*N*-tosylaziridine **1a** and propargyl alcohol **2a** in the presence of $[Ag(COD)_2]PF_6$ (2 mol %) in dichloroethane proceeded well at ambient temperature. At the consumption of **1a**, Cs_2CO_3 (1 equiv) was added and the reaction was continued at 80 °C leading to the formation of 1,4-oxazepine derivative **3** in 72% isolated yield (Scheme 2, Table 1).

SCHEME 2



(10) Selected examples of related multicomponent reactions: (a) Garner, P.; Kaniskan, H. U.; Hu, J.; Youngs, W. J.; Panzner, M. *Org. Lett.* **2006**, *8*, 3647. (b) Cui, S. L.; Wang, J.; Wang, Y. G. *Org. Lett.* **2007**, *9*, 5023. (c) Kim, J. T.; Gevorgyan, V. *Org. Lett.* **2002**, *4*, 4697. (d) Yan, B.; Liu, Y. *Org. Lett.* **2007**, *9*, 4323. (e) Cui, S. L.; Lin, X. F.; Wang, Y. G. *Org. Lett.* **2006**, *8*, 4517. (f) Lin, C. C.; Teng, T. M; Odedra, A.; Liu, R. S. *J. Am. Chem. Soc.* **2007**, *129*, 3798. (g) Xu, X.; Cheng, D.; Li, J.; Guo, H.; Yan, J. *Org. Lett.* **2007**, *9*, 1585.

(11) A few recent examples: (a) Binder, J. T.; Kirsch, S. F. *Org. Lett.* **2006**, *8*, 2151. (b) Godet, T.; Vaxelaire, C.; Michel, C.; Milet, A.; Belmont, P. *Chem.—Eur. J.* **2007**, *13*, 5632. (c) Su, S.; Porco, J. A., Jr. *J. Am. Chem. Soc.* **2007**, *129*, 7744. (d) Bobeck, D. R.; Warner, D. L.; Vedejs, E. *J. Org. Chem.* **2007**, *72*, 8506. (e) Chen, Z.; Yang, X.; Wu, J. *Chem. Commun.* **2009**, 3469. (f) Blanc, A.; Tenbrink, K.; Weibel, J. M.; Pale, P. *J. Org. Chem.* **2009**, *74*, 4360.

(12) (a) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics* **1999**, *18*, 2782. (b) Kundu, A.; Roy, S. *Organometallics* **2000**, *19*, 105. (c) Banerjee, M.; Roy, S. *Chem. Commun.* **2003**, 534. (d) Banerjee, M.; Roy, S. *Org. Lett.* **2004**, *6*, 2137.

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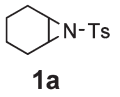
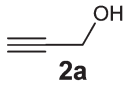
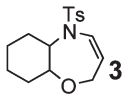
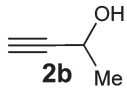
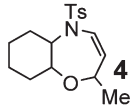
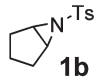
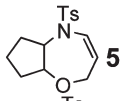
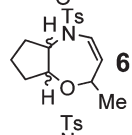
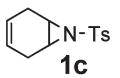
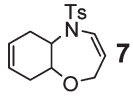
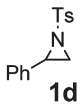
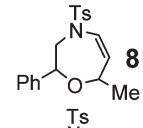
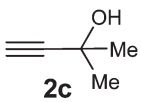
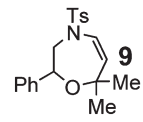
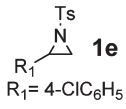
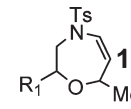
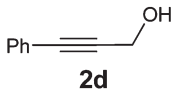
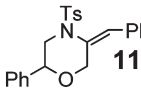
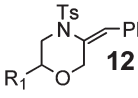
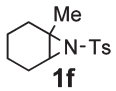
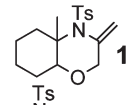
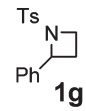
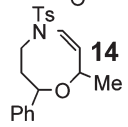
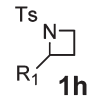
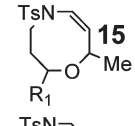
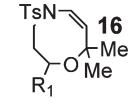
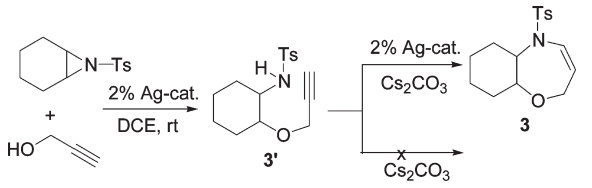
TABLE 1. $[Ag(COD)_2]PF_6$ Catalyzed Ring-Opening/Ring-Closing of Aziridines and Azetidines with Propargyl Alcohol[a]

#	Aziridine	Propargyl alcohol	Product	Yields (%)[b]
1	 **1a**	 **2a**	 **3**	72
2	**1a**	 **2b**	 **4**	70
3	 **1b**	**2a**	 **5**	68
4	**1b**	**2b**	 **6**	71
5	 **1c**	**2a**	 **7**	70
6	 **1d**	**2b**	 **8**	75
7	**1d**	 **2c**	 **9**	76
8	 **1e** R_1= 4-ClC_6H_5	**2b**	 **10**	75
9	**1d**	 **2d**	 **11**	70
10	**1e**	**2d**	 **12**	68
11	 **1f**	**2a**	 **13**	66
12	 **1g**	**2b**	 **14**	65
13	 **1h**	**2b**	 **15**	63
14	**1h**	**2c**	 **16**	63

[a]Conditions: *N*-tosylaziridine (0.5 mmol), propargyl alcohol (0.5 mmol), and $[Ag(COD)_2]PF_6$ (2 mol %), dry dichloroethane (2 mL) Cs_2CO_3 (1 equiv). [b]Isolated yield.

Control studies (Scheme 3 and Supporting Information Scheme S1 and Table S1)[15] indicated that (i) the optimum catalyst loading is 2 mol %; (ii) the reaction proceeds with $AgPF_6$, $AgSbF_6$, and $AgBF_4$ as the catalyst albeit with poorer yield of the product; (iii) other silver salts such as $AgNO_3$,

SCHEME 3



Ag_2CO_3, Ag_2SO_4, and AgCl do not promote any reaction; (iv) the product of the first catalytic event, namely 4-methyl-*N*-(2-propargyloxycyclohexyl)benzene sulfonamide **3′**, was isolated in 80% yield simply by quenching the reaction after 1 h; (v) the dual combination of $[Ag(COD)_2]PF_6$ and Cs_2CO_3 efficiently promoted the ring-closing of **3′** to **3**; and (vi) Cs_2CO_3 alone cannot promote the formation **3** and **3′** (Scheme 3). All of the above observations highlight the unique role of Ag(I) in this novel cascade reaction.

It is worth mentioning here that while this work was nearing completion, two reports on coupling between arylpropargyl alcohols and aziridines have appeared. However, we would like to emphasize that in sharp contrast to our results, (a) stoichiometric *t*-BuOK promoted coupling gave rise to exclusive formation of endocyclic morpholines,[16a] while (b) catalytic $Yb(OTf)_3$ promoted coupling yielded exclusively indene derivatives.[16b]

The cascade coupling has been satisfactorily extended to various propargyl alcohols, and substituted *N*-tosyl aziridines/azetidines leading to the selective formation of a diverse range of *N*,*O*-heterocycles, namely 1,4-oxazepines, 1,5-oxazocines, and 1,4-oxazines (Scheme 2, Table 1). *N*-Tosylaziridines having an alkyl or aryl appendage smoothly reacted with propargyl alcohols with terminal acetylenic linker to provide the corresponding 1,4-oxazepines **3**−**10** as the exclusive product (entries 1−8). Note that oxazepine **6** is obtained as a *cis*−*trans* mixture (1:1) possibly due to the conformational equilibrium of the fused 5- to 7-member bicyclic ring system (entry 4). Interestingly the reaction could be tuned to give 1,4-oxazines **11**−**13** by employing either a propargyl alcohol having internal acetylenic linker (entries 9 and 10), or by increasing the steric crowding around the aziridine framework (entry 11).

As discussed later, the formation of oxazepines and oxazines above is the outcome of the ring-closing step. Gratifyingly, we could also employ *N*-tosylazetidines in the present cascade coupling reaction to provide the corresponding 1,5-oxazocine derivatives **14**−**16** in moderate yields (entries 12−14).

While mechanistic details must await further studies, a proposal on the reaction course is presented in Scheme 4. The initial event will involve activation of the heteroatoms of the substrates by $[Ag(COD)]^+$.[17] This will facilitate the opening of the aziridine/azetidine ring. π-Activation and metallotropic rearrangement of **17** is expected to result in the formation of intermediates Ag(I)−alkyne **17a**, and Ag(I)−allene **17b**. When assisted by a base, the ring-closing event from **17a** and **17b** may follow *endo-dig* (path a, path c) or *exo-dig*/*trig* (path b, path d) pathways—subsequent protodemetalation would afford the organic product and regenerate the Ag(I) catalyst. It is point worthy that ring-closure via path a involving 7-*endo-dig* or 8-*endo-dig* mode and path c involving 6-*endo-dig* mode are favored by Baldwin's rule. Indeed the observed formation of 1,4-oxazepines, 1,5-oxazocines, and 1,4-oxazines in our hand conforms to the above selection rules. Path b involving ring-closure in a 6-*exo-dig* manner is disfavored. Although the 5-*exo-trig* mode (path d) for the plausible formation of oxazolidine **25** is favored, we could not observe its formation.

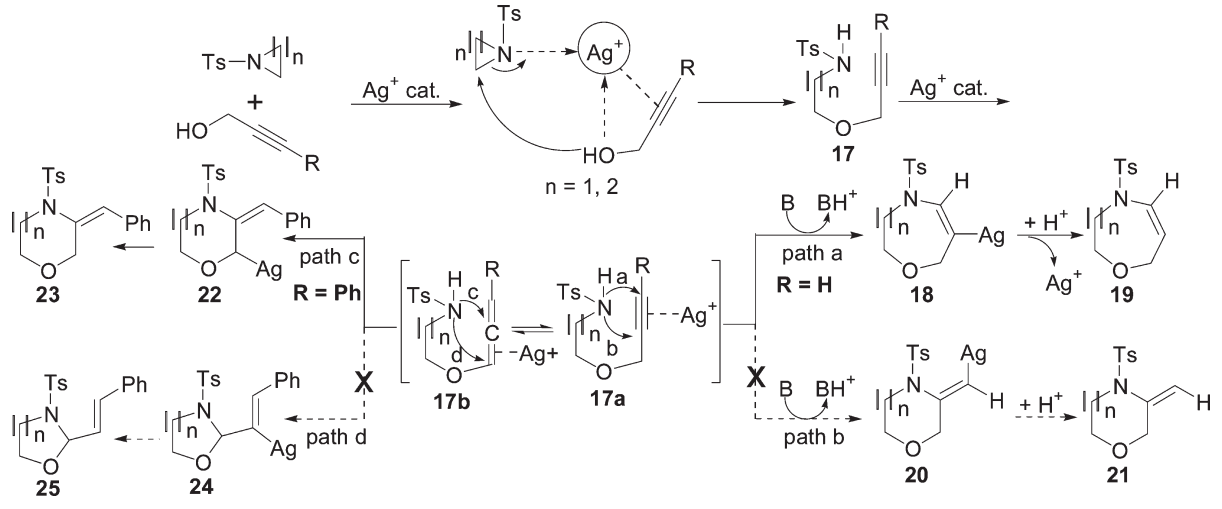
In conclusion, we have presented a novel approach for the preparation of 6-, 7-, and 8-member unsaturated heterocycles having two heteroatoms through a Ag(I)-catalyzed cascade reaction of aziridines/azetidines with propargyl alcohols. Further work is underway in our laboratory to broaden the scope of the reaction, and to explore the mechanism.

Experimental Section

All reactions were carried out under an argon atmosphere in flame-dried glassware with Schlenk techniques. Chromatographic purifications were done with either 60−120 or 100−200 mesh silica gel. For reaction monitoring, precoated silica gel 60 F_{254} TLC sheets were used. Petroleum ether refers to the fraction boiling in the range 60−80 °C. Dichloroethane was dried and distilled prior to use.

Preparation of $[Ag(COD)_2]PF_6$. To a water solution of $AgPF_6$ (0.5 mmol in 3 mL of water) was added a methanolic solution of

SCHEME 4



1,5-cyclooctadiene (2 mmol in 0.5 mL of methanol) at room temperature in the absence of light. Reaction was completed just after 5 min and the residue was filtered and washed with water and hexane. The white solid was then dried under vacuum. It was then crystallized from benzene/ dichloromethane solvent system. Anal. Calcd for $C_{16}H_{26}OAgPF_6$: C, 39.44; H, 5.38. Found: C, 39.46; H, 5.04. MS (*m*/*z*) $[Ag(C_8H_{12})_2]^+$ at 323 at cone voltage 15 V, $[Ag(C_8H_{12})]^+$ at 215 at cone voltage 35 V.

General Procedure. A mixture of *N*-tosylaziridine (0.5 mmol), propargyl alcohol (0.5 mmol), and $[Ag(COD)_2]PF_6$ (2 mol %) in 2 mL of dry dichloroethane was stirred at room temperature. After 1−3 h (vide TLC), when aziridine was nearly diminished then Cs_2CO_3 (1 equiv) was added and the reaction mixture was heated at 80 °C for 3−5 h. After completion of the reaction (vide TLC) the mixture was diluted with water (5 mL) and extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuum, then the resulting product was purified by column chromatography on silica gel (100−200 mesh, ethyl acetate−petroleum ether, 1:5 v/v) to afford the corresponding heterocycles in good yields.

(15) See the Supporting Information for details.

(16) (a) Wang, L.; Liu, Q. B.; Wang, D. S.; Li, X.; Han, X. W.; Xiao, W. J.; Zhou, Y. G. *Org. Lett.* **2009**, *11*, 1119. (b) Wang, S.; Zhu, Y.; Wang, Y.; Lu, P. *Org. Lett.* **2009**, *11*, 2615.

(17) ESI-MS spectrum of $[Ag(COD)_2]PF_6$ in ES(+) mode showed peaks corresponding to both $[Ag(COD)_2]^+$ and $[Ag(COD)]^+$ at low cone voltage (15 V). On the other hand at high cone voltage (35 V), $[Ag(COD)]^+$ was the only species present. This suggests the lability of $[Ag(COD)_2]^+$ in solution. Note that the metal−olefin bond distance in $[Ag(COD)_2]PF_6$ (2.50 Å) is longer compared to other d^{10} analogues such as Cu, Ni, and Pt; see: (a) Vander, J.; Hende, H.; Baird, W. C. *J. Am. Chem. Soc.* **1963**, *85*, 1003. (b) Schunn, R. A.; Ittel, S. D.; Cushing, M. A. *Inorg. Synth.* **1990**, *28*, 94. (c) Howard, J. A. K. *Acta Crystallogr.* **1982**, *B38*, 2896.

Preparation of 5-Tosyl-2,5,5a,6,7,8,9,9a-octahydrobenzo[*b*]-[1,4]oxazepine [3]. A mixture of *N*-tosylcyclohexyl aziridine (0.5 mmol, 125 mg), propargyl alcohol (0.5 mmol, 30 μL), and $[Ag(COD)_2]PF_6$ (0.01 mmol, 4.6 mg) in 2 mL of dichloroethane was stirred at room temperature. After 1 h when aziridine was totally diminished Cs_2CO_3 (0.5 mmol, 163 mg) was added and the reaction mixture was heated at 80 °C for 3 h. After completion of the reaction (vide TLC), the reaction mixture was diluted with water (5 mL) and extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuum, then the resulting product was purified by column chromatography on silica gel (100−200 mesh, ethyl acetate−petroleum ether, 1:5). The yield was obtained in 72% (110.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31−1.46 (m, 4H), 1.68−1.75 (m, 2H), 1.92 (t, J = 5.2 Hz, 1H), 2.28−2.32 (m, 1H), 2.39 (s, 3H), 3.20−3.26 (m, 1H), 3.60−3.66 (m, 1H), 3.89−4.02 (m, 2H), 4.98−5.01 (m, 1H), 6.28 (d, J = 9.2 Hz, 1H), 7.25 (d, J = 8 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.8, 29.7, 33.3, 34.6, 67.9, 69.2, 78.4, 120.5, 124.9, 127.2, 129.3, 136.3, 143.2; DEPT-135 NMR 21.6 (CH_3), 24.8 (CH_2), 29.7 (CH_2), 33.2 (CH_2), 34.6 (CH_2), 67.9 (CH), 69.2 (CH_2), 78.3 (CH), 120.6 (CH), 124.8 (CH), 127.2 (CH), 129.4 (CH). Anal. Calcd for $C_{16}H_{21}NO_3S$: C, 62.51; H, 6.89; N, 4.56. Found: C, 62.49; H, 6.92; N, 4.54.

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Supporting Information Available: Experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra for all new compounds and crystallographic data for **4**, **9**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.