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Silver(I)-Catalyzed Tandem 1,3-Acyloxy Migration/Mannich-type Addition/Elimination of the Sulfonyl Group of *N*-Sulfonylhydrazone-propargylic Esters to 5,6-Dihydropyridazin-4-one Derivatives

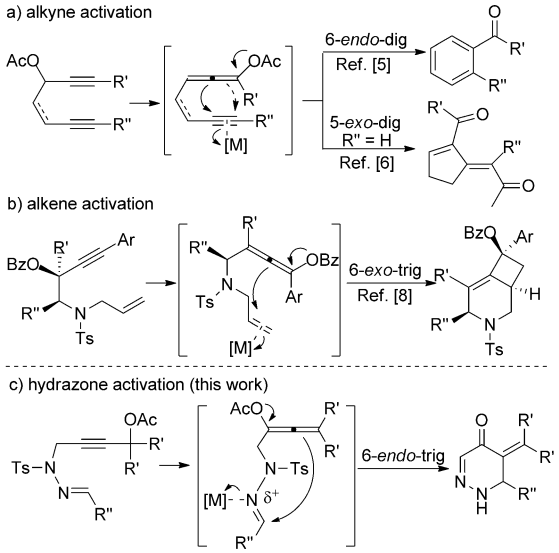
Zhen Zhang[a] and Min Shi*[a, b]

Abstract: The addition of nucleophiles to C=N bonds offers a highly efficient synthetic strategy for accessing nitrogen-containing molecules.[1] Among the well-developed addition reactions, such as the highly efficient Mannich reaction, various C–H bond-activated compounds including carboxylic acid derivatives, nitroalkanes, and terminal alkynes have been applied as nucleophiles to achieve different classes of amines.[2] However, employing new nucleophiles without activated C–H bonds, such as internal alkynes and allenic esters are limited when using metal catalysts.[3] Herein, we wish to report a new addition of allenic esters to C=N bonds initiated by a silver-catalyzed 1,3-migration of propargylic esters.

Keywords: Mannich reaction · propargylic esters · silver · sulfonylhydrazones · tandem reaction

Introduction

In the context of gold or silver catalysis, propargylic esters have highly valuable reactivity to undergo 1,2- or 1,3-acyloxy migration, leading to the formation of a metal–carbene or an allenic intermediate.[4] In the case of further transformation arising from 1,3-migration, selective coordination of the metal catalyst to the pendant functional group rather than the allenic moiety is a challenge. In this aspect, Toste's group explored a silver-catalyzed tandem 1,3-acyloxy migration/formal Myers–Saito cyclization of diynyl esters to form aromatic ketones,[5] and Malacria and his co-workers reported a gold-catalyzed cyclization of diynyl esters led to diketones after 1,3-acyloxy migration/5-*exo*-dig cyclization/1,5-acyl migration (Scheme 1a).[6] Our group has also developed a gold(I)-catalyzed tandem Meyer–Schuster-like rearrangement/5-*endo*-dig cycloaddition of diynyl esters to afford 2,3-disubstituted 3-pyrrolines in good yields.[7] Although diynyl esters are very efficient in this transformation, other substrates bearing no diyne moiety are still not known until Chan's group recently reported a gold-catalyzed tandem 1,3-acyloxy migration/[2+2]-cycloaddition of 1,7-enyne benzoates (Scheme 1b).[8,9] In the light of these findings, an efficient method for the preparation of 5,6-dihydropyridazin-4-one derivatives, a class of new compounds that have been seldom reported in the previous literature,[10–11] based on a silver-catalyzed tandem 1,3-acyloxy migration/Mannich-type addition/elimination of the sulfonyl group of *N*-sulfonylhydrazone-propargylic esters, has been disclosed (Scheme 1c).[12]



Scheme 1. Distinct cyclization modes for various propargylic esters: a) through alkyne activation; b) through alkene activation; c) through hydrazone activation. M = Au or Ag.

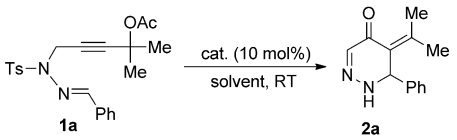
Initially, we started the optimization of the reaction conditions by using (*E*)-5-(2-benzylidene-1-tosylhydrazinyl)-2-methylpent-3-yn-2-yl acetate (**1a**) and $AgSbF_6$ (10 mol%) in wet dichloromethane at room temperature; the desired

[a] Z. Zhang, M. Shi
Laboratory for Advanced Materials & Institute of Fine Chemicals, East China University of Science and Technology
130 Mei Long Road, Shanghai 200237 (P.R. China)

[b] M. Shi
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
354 Fenglin Road, Shanghai 200032 (P.R. China)
Fax: (+86) 21-64166128
E-mail: Mshi@mail.sioc.ac.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201103404. It contains experimental procedures, compound characterization data, and X-ray crystal data of **2a**, **3c**, and **5b**.

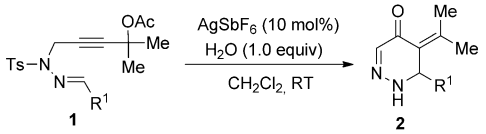
Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Additive [(equiv)]	Solvent	t [h]	Yield[b] [%]
1	$AgSbF_6$	–	CH_2Cl_2	2	79
2	AgOTf	–	CH_2Cl_2	2.5	38
3	$AgBF_4$	–	CH_2Cl_2	2	64
4	AgOAc	–	CH_2Cl_2	24	n.r.[c]
5	$AgSbF_6$	–	$ClCH_2CH_2Cl$	2	61
6	$AgSbF_6$	–	toluene	2.5	42
7	$Au(PPh_3)Cl/AgSbF_6$	–	CH_2Cl_2	3.5	19
8	TfOH	–	CH_2Cl_2	24	n.r.[c]
9	$BF_3{\cdot}Et_2O$	–	CH_2Cl_2	24	n.r.[c]
10	$Sc(OTf)_3$	–	CH_2Cl_2	24	n.r.[c]
11	$AlCl_3$	–	CH_2Cl_2	24	n.r.[c]
12	$AgSbF_6$	–	dry CH_2Cl_2	3	–[d]
13	$AgSbF_6$	H_2O (1.0)	dry CH_2Cl_2	1	84
14	$AgSbF_6$	H_2O (1.0)	dry CH_2Cl_2	1	84

[a] All reactions were performed on a 0.10 mmol scale. [b] Isolated product yield. [d] n.r. = no reaction. [d] Trace.

Table 2. Silver-catalyzed tandem reaction of *N*-sulfonylhydrazone-propargylic esters **1b–k**.[a]



Entry	Substrate	t [h]	Product	Yield[b] [%]
1	**1b**, $R^1 = 4\text{-}MeC_6H_4$	1	**2b**	60
2	**1c**, $R^1 = 4\text{-}MeOC_6H_4$	1	**2c**	30
3	**1d**, $R^1 = 4\text{-}BrC_6H_4$	3	**2d**	81
4	**1e**, $R^1 = 4\text{-}ClC_6H_4$	5	**2e**	65
5	**1f**, $R^1 = 4\text{-}CF_3C_6H_4$	5	**2f**	80
6	**1g**, $R^1 = 2\text{-}FC_6H_4$	6	**2g**	74
7	**1h**, $R^1 = 2\text{-}ClC_6H_4$	6	**2h**	73
8	**1i**, $R^1 = 2,3\text{-}Cl_2C_6H_3$	8	**2i**	70
9	**1j**, $R^1 = i\text{Pr}$	10	**2j**	0
10	**1k**, $R^1 = 2\text{-furan}$	5	**2k**	0[c]

[a] Conditions: **1**, $AgSbF_6$ (10 mol%), H_2O (1.0 equiv), CH_2Cl_2, RT. [b] Isolated product yield. [c] For details, see the Supporting Information.

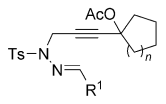
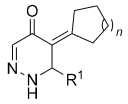
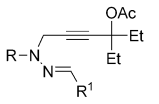
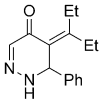
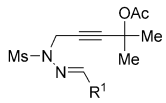
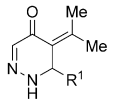
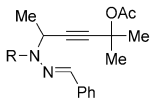
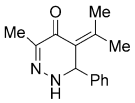
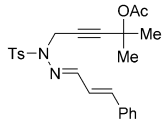
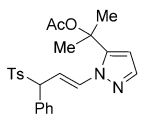
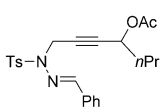
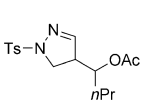
product 6-phenyl-5-(propan-2-ylidene)-5,6-dihydropyridazin-4(1*H*)one (**2a**) was formed in 79% yield after 2 h (Table 1, entry 1). The structure of **2a** has been unequivocally confirmed by X-ray diffraction.[13] Other silver catalysts, such as AgOTf, $AgBF_4$, and AgOAc did not give better results than $AgSbF_6$ (Table 1, entries 2–4). Other solvents were also tested in the reaction. The desired product **2a** was formed in 61 and 42% yields in 1,2-dichloroethane and toluene, respectively (Table 1, entries 5 and 6). The combined catalyst $Au(PPh_3)Cl/AgSbF_6$, Brønsted acid trifluoromethanesulfonic acid (TfOH), and Lewis acids, such as $BF_3{\cdot}Et_2O$, $Sc(OTf)_3$, and $AlCl_3$, have also been applied to the reaction, but no superior results were obtained (Table 1, entries 7–11). To investigate the additive affect of water in this transformation, dry dichloromethane was used in this reaction under the standard conditions, giving **2a** in trace amounts (Table 1, entry 12). When using dry dichloromethane containing 1.0 or 2.0 equivalents of water, the reaction was accelerated and an 84% yield of **2a** was obtained after 1 h (Table 1, entries 13 and 14). Thus, the use of $AgSbF_6$ (10 mol%) as the catalyst and 1.0 equivalent of water as the additive in dry dichloromethane at room temperature has been identified as the optimal reaction conditions.

Under the optimized conditions, we next investigated the tolerance of silver(I)-catalyzed tandem cyclization of various hydrazones **1b–k** and the results are shown in Table 2. As for substrates **1b** and **1c** bearing electron-donating groups (methyl or methoxy group) on their benzene rings, the corresponding products **2b** and **2c** were obtained in 60 and 30% yields, respectively (Table 2, entries 1 and 2). The poor yield of **2c** is presumably due to the electronic effect because many unidentified by-products were observed in the reaction. As for substrates **1d–i** bearing electron-withdrawing groups (fluoride, chloride, bromide, or trifluoromethyl group) on their benzene rings, the reactions proceeded smoothly to give the desired products **2d–i** in 65–81% yields at room temperature (Table 2, entries 3–8). On the basis of the results, it could be seen that the *ortho*- or *para*-substitution on the aromatic ring did not significantly interfere with the reaction outcomes. The hydrazone possessing an alkyl group **1j** was also tested, but none of the corresponding product was observed with all the starting materials recovered (Table 2, entry 9). For the 2-furan-substituted hydrazone **1k**, the corresponding product **2k** was not obtained and the 1,3-migration product was formed (Table 2, entry 10, see the Supporting Information).

Furthermore, to extend the scope of this reaction, we investigated a range of propargylic esters tethered with hydrazones **1l–v** and the results of these experiments are summarized in Table 3. For propargylic esters substituted with a subcycloalkyl group (compounds **1l–n**), the expected products **2l–n** were obtained in 55–66% yields under the standard conditions. When an alkylsulfonyl group was introduced to the substrate instead of the tosyl group, the reactions also proceeded smoothly to give the corresponding products in good yields (substrates **1p–t**). Introducing a methyl group to propargylic hydrazone (substrates **1s** and **1t**), the corresponding 3-substituted 5,6-dihydropyridazin-4-one **2s** could be also formed in 30 and 44% yields, respectively. For styrenyl hydrazone **1u**, the pyrazole **3a** was formed in 73% yield without the formation of the 5,6-dihydropyridazin-4-one product. As for substrate **1v**, which contains a hydrogen atom at the terminal of the alkyne moiety, 4,5-dihydropyrazole **3b** was obtained in 41% yield.[14] Other substrates, such as **1w** tethered by an oxygen atom, gave no reaction under the standard conditions (see the Supporting Information).

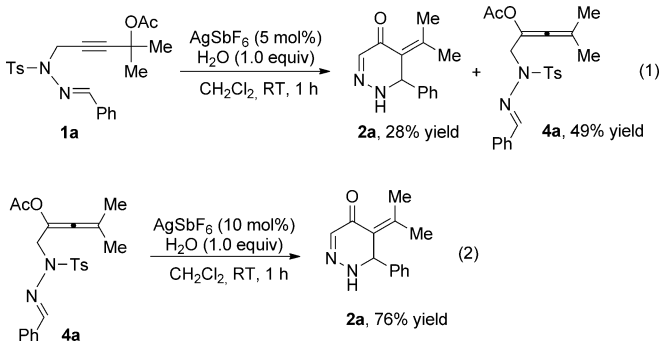
To verify the reaction pathway, the control experiment has been performed upon treating **1a** with the decreased silver catalyst loading (5 mol%) and it was found that **2a**

Table 3. Scope of the silver-catalyzed tandem reaction of *N*-sulfonylhydrazone-propargylic esters.[a]

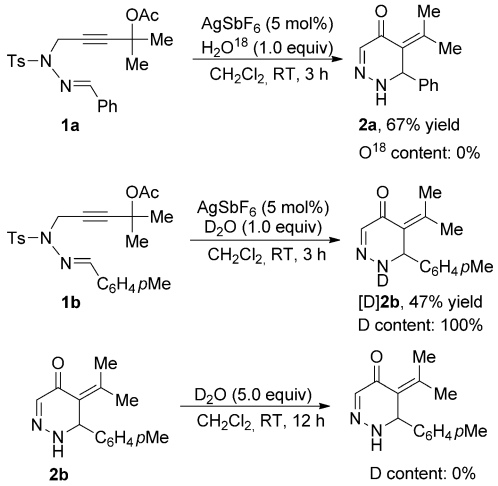
Substrate	Product[b]	Substrate	Product[b]
			
1l, $n=1$, $R^1=4$-ClC_6H_4	**2l** (1 h, 55%)	**1o**, R = Ts	**2o** (4 h, 80%)
1m, $n=2$, $R^1=C_6H_5$	**2m** (1 h, 66%)	**1p**, R = Ms	**2o** (2 h, 88%)
1n, $n=3$, $R^1=C_6H_5$	**2n** (4 h, 64%)		
			
1q, $R^1=C_6H_5$	**2a** (3 h, 70%)	**1s**, R = Ms	**2s** (5 h, 44%)
1r, $R^1=4$-ClC_6H_5	**2e** (3 h, 62%)	**1t**, R = $EtSO_2$	**2s** (3 h, 30%)
			
1u	**3a** (4 h, 73%)	**1v**	**3b** (24 h, 41%)

[a] Conditions: **1**, $AgSbF_6$ (10 mol%), H_2O (1.0 equiv), CH_2Cl_2, RT. [b] Reaction time and isolated product yield.

could be obtained in 28% yield along with the formation of 3,3-sigmatropic rearrangement product **4a** in 49% yield after 1 h (see reaction (1)). Subjecting **4a** to the reaction under the standard conditions, **2a** was formed in 76% yield, which indicated that compound **4a** might be the intermediate of this reaction (see reaction (2)).



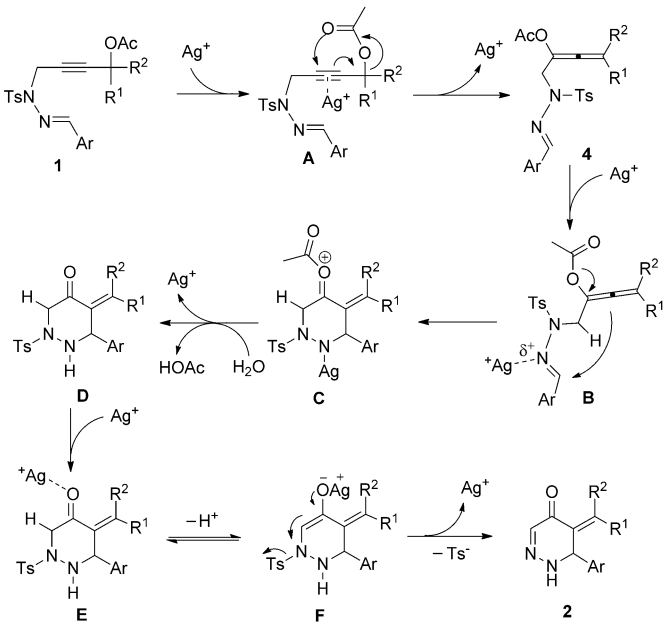
Moreover, isotope labeling experiments have been also performed (Scheme 2). By using **1a** as the substrate with addition of 1.0 equivalent H_2O^{18} to the reaction mixture, it was found that **2a** was formed in 67% yield along with 0% of ^{18}O content (determined by EI-MS analysis, see the Supporting Information), which indicated that the oxygen atom of product **2a** is derived from substrate **1a** and no Meyer–Schuster rearrangement occurred in the cyclization.[15] The deuterium-labeling experiment was carried out by using **1b** as the substrate in the presence of 1.0 equivalent of D_2O under the standard conditions. The corresponding product



Scheme 2. Isotopic labeling experiments.

[D]**2b** was formed in 47% yield along with 100% D content in the nitrogen proton. However, treating **2b** with 5.0 equivalents of D_2O in dichloromethane did not afford [D]**2b**, supporting the hydrogen transfer from water to the final product **2**.

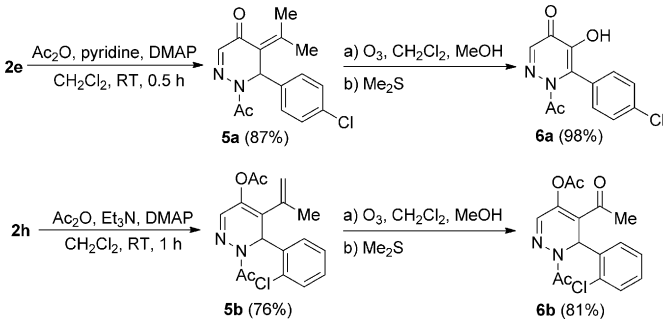
On the basis of above experiments, a plausible reaction mechanism is outlined in Scheme 3. The cationic silver(I) first coordinates to the alkyne moiety of **1** to afford intermediate **A**, which undergoes a 3,3-sigmatropic rearrangement to give carboxyallene intermediate **4**.[16] Activation of the hydrazone sp^2 nitrogen atom of **4** by silver(I) produces intermediate **B**,[17] which induces a Mannich-type addition of the allenic acetate to the C=N bond to give intermediate **C**.



Scheme 3. Plausible reaction mechanism.

In the presence of water, intermediate **C** undergoes hydrolysis to give intermediate **D** and regenerates the silver(I) catalyst. Then the carbonyl group of intermediate **D** is activated by cationic silver(I), affording intermediate **E**, which undergoes a soft enolization to give intermediate **F**.[18] Release of the tosyl moiety of **F** produces the product **2**.[19]

The transformation of the product 5,6-dihydropyridazin-4-one **2** to other pyridazin derivatives was briefly examined (Scheme 4). Compound **2e** was readily converted into the



Scheme 4. The transformation of **2** to pyridazin derivatives **5** and **6**. DMAP = 4-dimethylaminopyridine.

N-acetylated product **5a** in the presence of acetic anhydride when pyridine was used as the base. However, when triethylamine was used instead of pyridine, the base could deprotonate the C–H bond of the methyl group to promote enolization, which was followed by acetylation to form the product **5b**. The structure of **5b** has been ascertained by X-ray diffraction.[13] By a conventional O_3 oxidation procedure, compound **5a** could be readily converted to 5-hydroxypyridazin-4-one **6a** and compound **5b** could be easily transformed to 1,6-dihydropyridazin **6b**, respectively.

In conclusion, we have developed a silver-catalyzed intramolecular transformation of propargylic esters with *N*-sulfonylhydrazones to give 5,6-dihydropyridazin-4-one derivatives in moderate to good yields under mild conditions. This new reaction procedure involved a tandem 1,3-acyloxy migration/Mannich-type addition/elimination of the sulfonyl group sequence. This new synthetic strategy based on an unprecedented addition of allenic ester to C=N bonds presents facile construction of pyridazin derivatives, which are not easily available by other methods. Further applications of propargylic esters in silver or gold catalysis and the more detailed investigation of the related reactions are underway in our laboratory.

Experimental Section

General information: Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J* values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Commercially obtained reagents were used without further purification. Dichloromethane was distilled from calcium hydride under argon. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out by using 300–400 mesh silica gel at increased pressure.

General procedure for the preparation of compounds 2: Substrate **1** (0.15 mmol) and $AgSbF_6$ (5.1 mg, 0.015 mmol) were added to a flame-dried Schlenk flask. Then water (3 μL, 0.15 mmol) and dry CH_2Cl_2 (1.5 mL) were added sequentially. The reaction mixture was stirred at room temperature under argon. When the reaction was completed, the yellow mixture was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography eluting with petroleum and ethyl acetate (v/v, 5:1). Compound **2** could be afforded as a yellow solid or oil.

6-Phenyl-5-(propan-2-ylidene)-5,6-dihydropyridazin-4(1*H*)one (2a): Yellow solid; m.p. 125–127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.97 (3H, s), 2.33 (3H, s), 5.64 (1H, s), 6.67 (1H, s), 7.21–7.23 (2H, m), 7.26–7.34 ppm (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 22.6, 23.9, 59.8, 125.6, 126.3, 128.0, 128.9, 134.8, 138.8, 151.7, 179.3 ppm; IR (neat): $\tilde{\nu}$ = 3294, 2926, 2854, 1740, 1656, 1610, 1492, 1458, 1363, 1267, 1169, 1089, 1020 cm^{-1}; MS (%): *m*/*z*: 214 (10.33) $[M]^+$, 173 (3.21), 137 (100.00), 83 (9.93); HRMS (EI): *m*/*z*: calcd for $C_{13}H_{14}N_2O$: 214.1106 $[M^+]$; found: 214.1109.

CCDC-805834 (**2a**), -800969 (**3c**), and -845690 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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