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Synthesis of *cis*-3-Acyl-4-alkenylpyrrolidines via Gold(I)-Catalyzed Cycloisomerization Reaction of (*Z*)-8-Aryl-5-tosyl-5-azaoct-2-en-7-yn-1-ols

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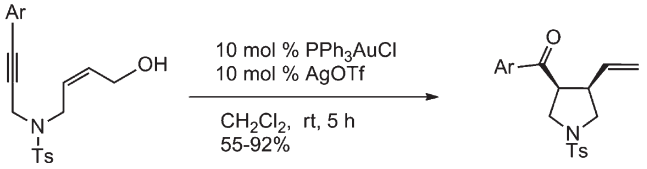

(*Z*)-8-Aryl-5-tosyl-5-azaoct-2-en-7-yn-1-ols were cycloisomerized to the corresponding *cis*-3-acyl-4-alkenylpyrrolidines when treated with a catalytic amount of Ph_3PAuCl/AgOTf in CH_2Cl_2. The reaction proceeded via attack of the hydroxyl group onto the gold-activated alkynes followed by [3,3]-sigmatropic rearrangement to generate *cis*-3-acyl-4-alkenylpyrrolidines in good yields. This transformation can be applied to the synthesis of *cis*- and *trans*-3-acyl-4-alkenylcyclopentanes from (*Z*)- and (*E*)-8-aryloct-2-en-7-yn-1-ols, respectively.

The construction of saturated nitrogen heterocyclic building blocks is an important synthetic goal because such ring skeletons are present in numerous natural products of biological interest.[1] Because the availability of functionalized nitrogen-containing 5-membered-ring building blocks could greatly facilitate the elaboration of more complex target molecules, the design of expedient synthetic routes to such intermediates has been actively pursued.[2−7] Many synthetic methods, as the key step, have been developed in pursuit of pyrrolidines, including intramolecular hydroamination of alkenes,[2] ring transformation of 2-(haloalkyl)azetidines,[3] Lewis acid-promoted [4 + 2] cycloaddition of 1-nitroalkenes with vinyl ethers,[4] and palladium-[5] and platinum-catalyzed[6] coupling reaction of N-sulfonated enynes. Among these, transition-metal-catalyzed coupling reaction of N-tethered enynes has received much attention as an atom-economical and expedient method to the synthesis of nitrogen heterocycles.[5,6] However, the Pd-catalyzed N-sulfonated cycloisomerization reaction of enynes required heating substrates at elevated temperature, and the Pt-catalyzed N-sulfonated coupling reaction of enynes gave only a trace amount of five-membered heterocycles. Recently, cationic phosphine gold(I) complexes have emerged as versatile catalysts for electrophilic activation of alkynes toward a variety of nucleophiles under mild reaction conditions, allowing numerous synthetic transformations of unsaturated systems into useful structure motifs.[7] In particular, gold-catalyzed intramolecular cyclization of allenes[8] and alkenes[2,9] tethered with nitrogen nucleophiles represents a common method for generation of pyrrolidines under mild reaction conditions. Although gold-catalyzed intramolecular amination of 1,5-enynes has been reported to give azabicyclic alkenes containing a pyrrolidine moiety,[10] a general gold(I)-catalyzed cycloisomerization of tosylamine-tethered 2-en-7-yn-1-ols to produce 3,4-disubsituted pyrrolidines in diastereselective fashion has yet to be developed. We have now demonstrated that phosphine gold(I) can be applied toward the stereospecific synthesis of pyrrolidines by treatment of (*Z*)-8-aryl-5-tosyl-5-azaoct-2-en-7-yn-1-ols with a catalytic amount of Ph_3PAuCl/AgOTf. In this transformation, a nucleophilic 9-*endo*-*dig* addition of the hydroxyl group onto the gold(I)-activated alkyne generated a cationic allylic vinyl ether gold intermediate. A subsequent Claisen-type rearrangement of the cyclic transient cationic intermediate produced a *cis*-3-acyl-4-alkenylpyrrolidine. Moreover, the gold(I)-catalyzed Claisen-type rearrangement of (*Z*)- and (*E*)-8-aryloct-2-en-7-yn-1-ols afforded *cis*- and *trans*-3-acyl-4-alkenylcyclopentanes, respectively.

The requisite (*Z*)-8-aryl-5-tosyl-5-azaoct-2-en-7-yn-1-ol **1** was prepared by addition of the corresponding (3-arylprop-2- yn-1-yl)tosylamine to (*Z*)-4-bromobut-2-en-1-yl acetate

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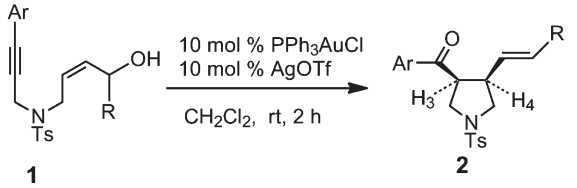
SCHEME 1. Gold(I)-Catalyzed Synthesis of *cis*-3-Acyl-4-alkenyl-pyrrolidines from (*Z*)-8-Aryl-5-tosyl-5-azaoct-2-en-7- yn-1-ols



a : Ar = Ph, R = H 87%
b : Ar = 4-methylphenyl, R = H 86%
c : Ar = 4-phenylphenyl, R = H 80%
d : Ar = naphthyl, R = H 77%
e : Ar = 4-methoxyphenyl, R = H 87%
f : Ar = 4-bromophenyl, R = H 92%
g : Ar = 4-nitrophenyl, R = H 55%
h : Ar = 4-carbethoxyphenyl, R = H 63%
i : Ar = Ph, R = Me 71%
j : Ar = Ph, R = CH_2Ph 51%
k : Ar = Ph, R = H 0%

followed by hydrolysis of the resulting acetates with K_2CO_3 in MeOH and H_2O to afford the desired tosylamine-tethered 2,7-enyn-1-ols **1** in good overall yields (Scheme 1). Treatment of the parent compound **1a** with 10 mol % of Ph_3PAuCl/AgOTf in CH_2Cl_2 at 25 °C for 2 h afforded *cis*-3-benzoyl-4-ethenyl-1-[(4-methylphenyl)sulfonyl]pyrrolidine (**2a**) as the sole diastereomer isolated in 87% yield. The relative stereochemistry of the side chains was determined as a *cis* relationship on the basis of ^1H NMR studies. The proton at δ 4.09 as a quartet in **2a**, J = 7.6 Hz, was assigned to H_3. The coupling constant of H_3-H_4 (J_{34}) of 7.6 Hz agrees with the 7.6−7.8 Hz coupling constant for the similar cis hydrogens found in the literature.[11] However, $PtCl_2$-catalyzed hydrative cyclization of tosylamine-tethered allenynes[12] and $[Rh(COD)_2]^+$-catalyzed cyclization/hydroboration of 1,6-enynes followed by oxidation[11] were both reported to give 3,4-disubstituted pyrrolidines as a mixture of cis and trans isomers. Thus, the current approach to the diastereoselective synthesis of 3,4-disubstituted pyrrolidines is achieved without the use of complex catalysts or critical reaction conditions, only requiring 10 mol % of Ph_3PAuCl/AgOTf in CH_2Cl_2 at room temperature. The investigation of various solvents in the presence of the gold(I) catalyst revealed that 1,2-dichloroethane (DCE) was also effective and gave the desired **2a** in 83% yield; the use of toluene did not give a better result (55%). More coordinating solvent such as THF and acetonitrile inhibited the reaction, and **2a** was isolated in low yields (6−10%). Moreover, no conversion of **1a** into **2a** was observed even after prolonged stirring in the presence of 10 mol % of $PtCl_2$ at elevated temperature in toluene. It is also known that TfOH-catalyzed cyclization reaction of a cyclic enynol, for example, 1-(5-phenylpent-4-yn-1-yl)cyclohex-2-en-1-ol, gave a spiro[5.4]decane.[13] The Brönsted acid catalyzed cyclization reaction was proposed to proceed by formation of an allylic cation that reacted as a strong electrophile with the pendant alkyne. To exclude the possibility of TfOH-catalyzed cyclization of **1a** to give **2a**, **1a** was treated with TfOH.

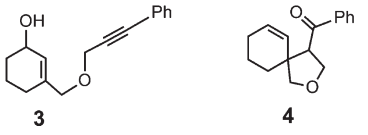
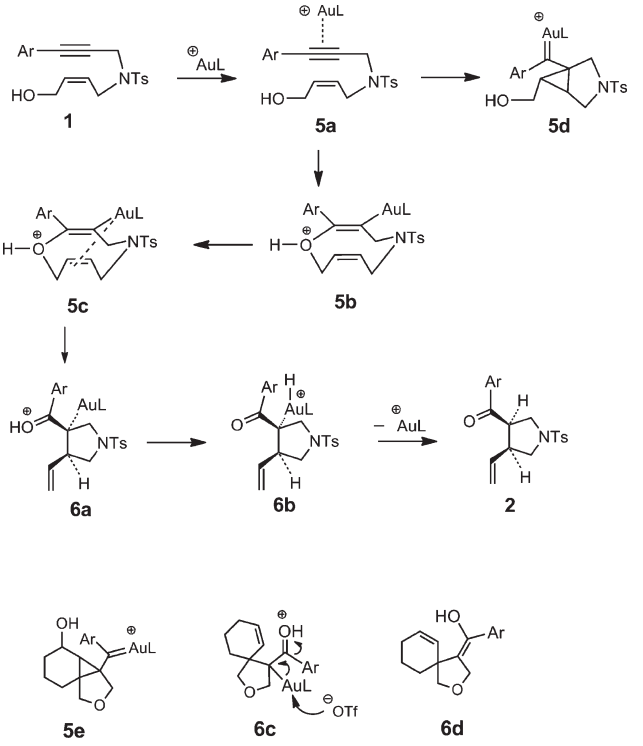


FIGURE 1. Compounds **3** and **4**.

SCHEME 2. Plausible Formation Mechanism of 2



However, compound **1a** decomposed immediately upon reaction with 10 mol % of TfOH in CH_2Cl_2 at room temperature. The failure of the reaction may provide evidence that the gold-catalyzed reaction did not proceed via an allylic carbocation. Recently, we have found that the cyclic 2,7-enyn-1-ol **3** (Figure 1), containing a very sensitive allyl propargyl ether moiety, converted smoothly into oxasiprocyclic ketone **4** using a catalytic amount of Ph_3PAuCl/AgOTf (5 mol %, CH_2Cl_2, 25 °C, 2 h, 62%),[14] while when treated with TfOH, compound **3** decomposed immediately. Therefore, a gold-activated intramolecular addition of the hydroxyl group to the pendant alkyne is likely to proceed. Moreover, treatment of the terminal alkyne **2k** with the gold cation failed to give pyrrolidines. A complex mixture of unidentified compounds and starting substrate **1a** were observed under the same reaction conditions. It was suggested that in the reaction of the terminal alkyne, the addition of the hydroxyl group may proceed in both 8-*exo-dig* and 9-*endodig* manners to give an unidentified mixture of oils. Thus, an aryl group at the alkyne terminus is required for the cycloisomerization. A reaction pathway was suggested in Scheme 2. The gold catalyst coordinated to the triple bond of **1** to give **5a**. Because of the significant carbocationic character at the alkynyl carbon

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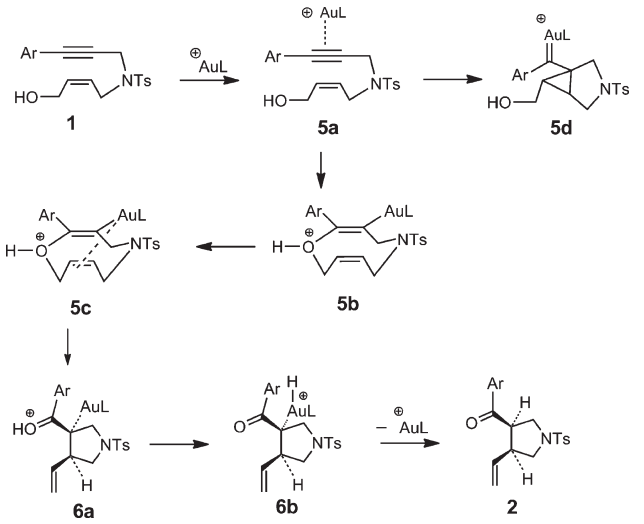
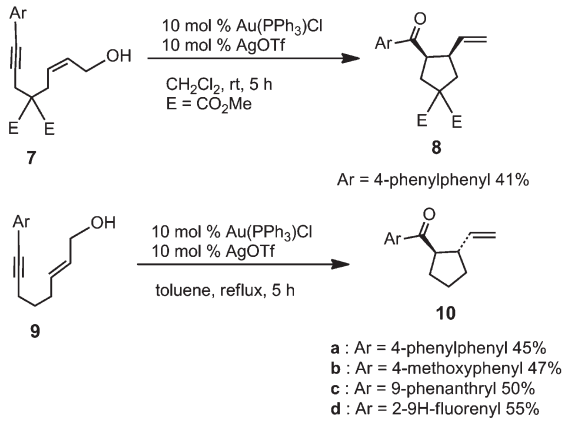


FIGURE 2. Compounds **5e**, **6c**, and **6d**.

(C(8)) adjacent to the aryl group, addition of the alcohol oxygen onto the C(8) in a 9-*endo-dig* fashion occurred to give **5b**. The gold catalyst completed its coordination sphere by complexation of the alkene to afford **5c**, and in this way it aligned the allylic and vinylic moieties for further conversion. A similar allylic vinyl gold complex was suggested in the literature as a low energy intermediate in the gold-catalyzed rearrangement of allenynes and N-allylic aminonitriles.[15] A subsequent Claisen-type rearrangement of the cyclic transient intermediate **5c** produced the *cis*-3,4-disubstituted pyrrolidine skeleton **6a**. Proton transfer (to give **6b**) followed by protodemetalation of **6a** afforded the pyrrolidine derivative **2** and regenerated the gold(I) catalyst in the catalytic cycle. However, in our previous study, attack of the triflate at the gold center of the cyclic intermediate **6c** would release steric congestion of the spiral skeleton and led to the formation of the spirocyclic enol **6d** (Figure 2). Enol **6d** led to spirocyclic ketones as a 1:1 mixture of diastereomers.[14] Although gold carbenoid **5d** has been suggested as a reactive intermediate in enyne cyclization, the lack of any observed formation of an alternative [3.1.0] bicyclic skeleton[7i] indicated that the cyclization is a 9-*endo-dig* cyclization. Moreover, cyclic substrate **3** gave **4** under the mild reaction conditions, suggesting that the cyclization was unlikely to proceed via the postulated steric demanding tricyclic goldcarbenoid intermediate **5e** (Figure 2).

The results of the gold-catalyzed cycloisomerization reaction of *cis*-8-aryl-5-tosyl-5-azaoct-2-en-7-yn-1-ols **1a**–**j** to produce *cis*-3-acyl-4-alkenylpyrrolidines **2a**–**j** are listed in Scheme 1.[16] Electron-neutral and -rich arenes at the alkyne terminus were proven to be good substrates, as the yields of the desired pyrrolidines **2a**–**e** ranged from 77% to 87%. In addition, the substrate with a para bromine atom at the phenyl ring, for example, **1f**, did not inhibit the catalytic activity of the gold species, as evidenced by a good yield of

SCHEME 3. Gold(I)-Catalyzed Synthesis of Cyclopentane Derivatives from 8-Aryloct-2,7-enyn-1-ols



product **2f** (92%). However, treatment of substrates **1g** and **1h** bearing an electron-withdrawing nitro or ester group at the para position of the arene was less effective and provided pyrrolidines **2g** (55%) and **2h** (63%), respectively. In both reactions, the starting substrates were recovered in 15–20% yields. The low yields of **2g**–**h** compared to those of **2a**–**e** may further support the fact that electron-neutral and -rich arenes play an important role in stabilizing the C(8). The relative stereochemistry of products **2a**–**j** was assigned as the same cis relationship between two hydrogen atoms at the two adjacent stereogenic centers on the basis of their close chemical shift values and similar coupling patterns of the protons in their ^{1}H NMR spectra. Secondary allylic alcohols **1i**–**j** also generated rearrangement products **2i**–**j** as the only diastereomer in each case and in 71% and 51% yields, respectively. Structural elucidation of pyrrolidines **2b**,**c**,**f**,**g**,**j** was achieved by X-ray crystallography. However, the tertiary allylic alcohol with two methyl groups on the C-1 position, for example, (*Z*)-1,1-dimethyl-8-phenyl-5-tosyl-5-azaoct-2-en-7- yn-1-ol, failed to generate the corresponding pyrrolidine using a high loading of the gold catalyst and elevated temperature. The failure of the cyclization might be attributed to an increased steric hindrance during the nucleophilic addition step of the hydroxyl group onto the gold(I)-activated alkyne.

The chemistry can be applied to synthesis of 1,2-disubstituted cyclopentanes from 8-aryloct-2-en-7-yn-1-ols. As shown in Scheme 3, this reaction proceeds with various (*Z*)- and (*E*)-8-aryloct-2-en-7-yn-1-ols in a stereospecific manner with high fidelity in transfer of stereochemical information. Thus, (*Z*)-8-aryloct-2-en-7-yn-1-ols with malonate as the tether, for example, **7**, were converted using the gold(I) catalyst (10 mol %) at room temperature for 5 h to the *cis*-3-acyl-4-ethenylcyclopentane derivative **8** in 41% yields. However, the reaction of (*E*)-8-aryloct-2-en-7-yn-1-ols **9a**–**d** with the gold(I) catalyst (10 mol %) was less efficient at room temperature. Thus, the reaction was performed in refluxing toluene for 6 h to give *trans*-3-acyl-4-ethenylcyclopentanes **10a**–**d** as the sole diastereomer in each case in 45–55% yields together with unidentified polymeric oils. The lack of a Thorpe–Ingold effect in cyclizations of **9a**,**b** to form five-membered rings[17] may allow intermolecular addition of the hydroxyl group to the gold-activated alkyne and gave fair yields of trans-1,2-disubstituted cyclopentanes **10a**,**b**. Structural elucidation

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of **10c** and **10d** was accomplished by X-ray diffraction analysis.

In summary, a gold(I)-catalyzed cycloisomerization reaction of (*Z*)-8-aryl-5-tosyl-5-azaoct-2-en-7-yn-1-ols has been successfully developed. The reaction proceeded via attack of the hydroxyl group onto the gold-activated alkyne followed by [3,3]-sigmatropic rearrangement to generate *cis*-3-acyl-4-alkenylpyrrolidines. This transformation can be applied to the synthesis of *cis*- and *trans*-3-acyl-4-alkenylcyclopentanes from (*Z*)- and (*E*)-8-aryloct-2-en-7-yn-1-ols, respectively.

Experimental Section

General Procedure for Gold(I)-Catalyzed Cycloisomerization Reaction of (*Z*)-8-Aryl-5-tosyl-5-azaoct- 2-en-7-yn-1-ols. A CH_2Cl_2 solution (5.6 mL) of (*Z*)-8-phenyl-5-tosyl-5-azaoct-2-en-7-yn-1-ol (**1a**) (0.20 g, 0.56 mmol) were added Ph_3PAuCl (0.028 g, 0.056 mmol) and AgOTf (0.019 g, 0.056 mmol) at room temperature under an atmosphere of nitrogen. The reaction mixture was stirred until all **1a** was consumed (typically 2 h). The reaction mixture was filtered through a bed of Celite and concentrated to give the crude mixture.

(±)-(3*S*,4*R*)-3-Benzoyl-4-ethenyl-1-[(4-methylphenyl)sulfonyl]-pyrrolidine (2a). The crude mixture from the cycloisomerization reaction of **1a** (0.20 g, 0.56 mmol) was purified by flash column chromatography[18] (silica gel, 10% ethyl acetate/hexanes) to give **2a** (0.17 g, 0.49 mmol, 87%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.26 (ddd, J = 16.8 Hz, J = 9.6 Hz, J = 9.6 Hz, 1H), 4.77 (d, J = 10.1 Hz, 1H), 4.72 (d, J = 17.0 Hz, 1H), 4.09 (q, J = 7.6 Hz, 1H), 3.74−3.60 (m, 3H), 3.28−3.24 (m, 1H), 3.23−3.19 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 143.5, 136.5, 133.7, 133.6, 133.3, 129.6, 128.6, 128.1, 127.5, 117.7, 52.8, 49.0, 48.3, 46.0, 21.4; IR (CH_2Cl_2) 3064, 2981, 2888, 1681, 1597, 1344, 1163 cm^{-1}; MS (EI) m/e 355.3 (M^+, 0.15), 223.1 (46), 201.2 (10), 200.2 (68), 155.1 (17), 146.1 (12), 105.1 (100), 91.1 (45), 77.1 (14), 68.1 (11), 67.1 (13), 65.1 (14); HRMS (EI) m/e calcd for $C_{20}H_{21}NO_3S$ 355.1242, found 355.1240.

(±)-(1*S*,2*R*)-1-Ethenyl-2-(9*H*-fluorenoyl-2-yl)cyclopentane (10d). The crude mixture from the cycloisomerization reaction of **9d** (0.28 g, 1.0 mmol) was purified by flash column chromatography[18] (silica gel, 3% ethyl acetate/hexanes) to give **10d** (0.16 g, 0.55 mmol, 55%) as a yellow solid: mp 67−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.99−7.97 (m, 1H), 7.81−7.78 (m, 2H), 7.54 (d, J = 7.2 Hz, 1H), 7.4−7.32 (m, 2H), 5.85 (ddd, J = 17.4, 10.2, 7.5 Hz, 1H), 5.01 (d, J = 17.1 Hz, 1H), 4.92 (dd, J = 10.2, 0.7 Hz, 1H), 3.9 (s, 2H), 3.58 (q, J = 8.2 Hz, 1H), 3.06 (p, J = 8.0 Hz, 1H), 2.13−1.7 (m, 5H), 1.61−1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 146.7, 145.0, 143.8, 141.8, 141.1, 136.2, 128.5, 128.4, 127.6, 125.8, 125.7, 121.4, 120.1, 114.6, 52.9, 47.9, 37.4, 33.5, 31.8, 25.6; IR(CH_2Cl_2) 3074, 2953, 1674, 1639, 1610, 1468, 1424 cm^{-1}; MS (EI) m/e 288.3 (M^+, 7), 194.2 (26), 193.2 (100), 193.2 (16), 166.2 (11), 165.1 (59); HRMS (EI) m/e calcd for $C_{21}H_{20}O$ 288.1511, found 288.1514. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of compounds **2a**−**j**, **8**, and **10a**−**d** and X-ray data for compounds **2b**,**c**,**f**,**g**, **j** and **10c**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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