Journal of Organometallic Chemistry 694 (2009) 482–485

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Communication

Gold(I)-catalyzed synthesis of (1*E*,3*E*)-dienes from propargylic esters

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ARTICLE INFO

Article history:
Received 24 May 2008
Received in revised form 6 August 2008
Accepted 6 August 2008
Available online 12 August 2008

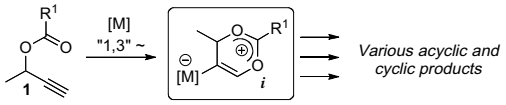
Keywords:
Gold
Homogeneous catalysis
Rearrangement
Propargylic esters
1,3-Dienes

ABSTRACT

A mild and stereoselective gold(I)-catalyzed domino transformation of propargylic esters leading to substituted (1*E*,3*E*)-dienes has been developed. This cascade process proceeds via a sequence of 1,3-acyloxy- or 1,3-phosphatyloxy migrations to form allenic intermediate followed by a proton transfer.

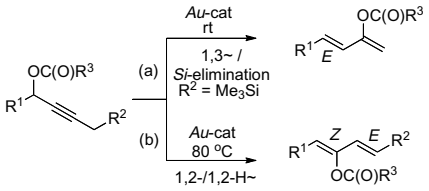
1. Introduction

During past decade, propargylic esters [1] have received much attention as a highly valuable building blocks in contemporary organic chemistry. Intriguing reactivity of these compounds in the context of gold catalysis [2] has been reflected in the development of a variety of diverse and elegant cascade transformations. Remarkable propensity of propargylic esters **1** to undergo a formal 1,3-acyloxy migration [1,2] through the activated allene equivalent, intermediate ***i*** [1], allowed for the development of diverse transformations for the expeditious assembly of an immense array of complex acyclic molecules [3], and multisubstituted carbo- [4] and heterocycles [5] (Eq. (1)).



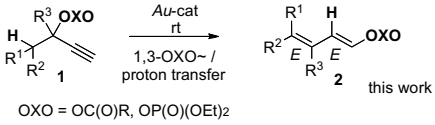
(1)

Recently, two stereoselective Au(I)-catalyzed isomerizations of propargylic esters into 2-oxy-1,3-diene esters [6], proceeding via a 1,3-migration – silicon elimination (Eq. (2), route a) [7] or double 1,2-migration (Eq. (2), route b) [8] tandems, were reported by Zhang.



(2)

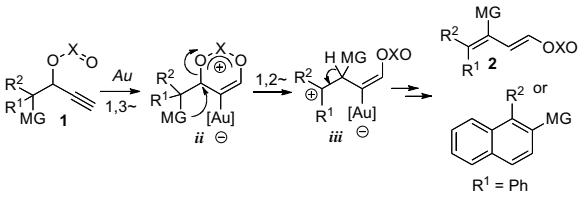
Herein, we wish to report a mild and stereoselective Au(I)-catalyzed 1,3-migration – proton transfer cascade of propargylic esters **1** into 1-oxy-(1*E*,3*E*)-diene esters **2** (Eq. (3)).



(3)

2. Results and discussion

Recently, we reported a Au(I)-catalyzed double 1,3-/1,2-migration cascade transformation of propargylic esters **1** into functionalized naphthalenes and 1,3-dienes (Eq. (4)) [9]. It was proposed that propargylic esters **1**, which are fully substituted at the β-position, underwent a Au(I)-catalyzed 1,3-acyloxy- or 1,3-phosphatyloxy group migration to give cyclic intermediate ***ii*** (Eq. (4)). The followed 1,2-migration of alkyl- or aryl group (MG = Alk, Ar) [10] in the latter



(4)

produced intermediate ***iii***, which, upon subsequent proton loss and protiodeauration, afforded 1,3-diene or underwent further cycloisomerization into the naphthalene core (Eq. (4)). In contrast, it was found that propargylic ester **1a**, possessing a hydrogen atom at the β-position, was transformed into (1*E*,3*E*)-diene **2a** via a sequence of two formal 1,3-migrations [9] (Eq. (5)).

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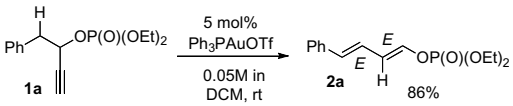
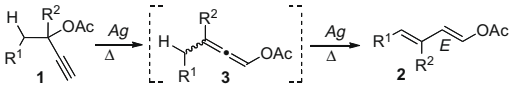
0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.08.010



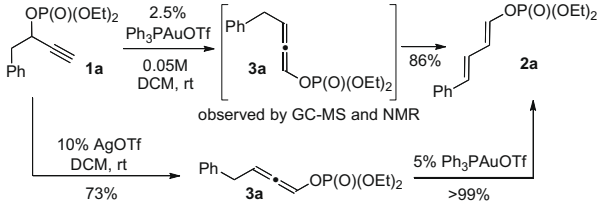
(5)

It deserves mentioning that the isomerization of acetates **1** into 1,3-dienes **2** in the presence of Ag-catalysts at elevated temperatures has been reported [11] (Eq. (6)). The cascade reaction was hypothesized to proceed via the allene intermediate **3**, though, the mechanism of this transformation remained unclear.



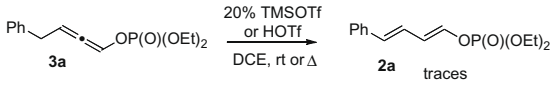
(6)

We aimed at elucidating whether the Au(I)-catalyzed isomerization of phosphate-containing substrate **1a** (MG = H) proceeds via an allenic intermediate. The performed careful monitoring of the reaction course at early stages revealed that, indeed, the corresponding allene intermediate **3a** was formed and then completely converted into (1*E*,3*E*)-diene **2a** (Eq. (7)). In addition, allene **3a**, prepared independently via the Ag-catalyzed 1,3-migration protocol, in the presence of cationic Au(I) triflate was quantitatively transformed into 1,3-diene **2a** (Eq. (7)).



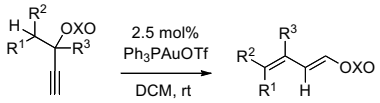
(7)

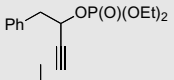
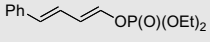
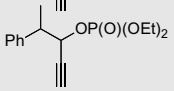
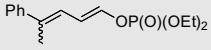
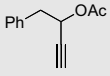
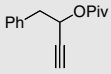
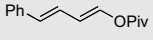
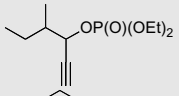
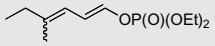
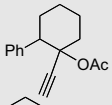
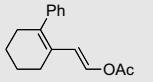
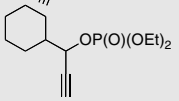
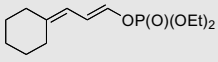
In light of the recent observations that eventual Brønsted acids are the true catalysts in some transition metal-catalyzed transformations [12], we investigated what role, if any, Brønsted or Lewis acids may play in the herein described isomerization reaction. It was found that isomerization of propargyl phosphate **1a** in the presence of 20 mol% of TfOH or TMSOTf provided no 1,3-diene **2a**. In addition, isomerization of the allene **3a** into the corresponding 1,3-diene in the presence of Brønsted or Lewis acids even at elevated temperatures resulted in trace amounts of **2a** only (Eq. (8)). Thus, the observed reactivity for the Au(I) catalyst cannot be attributed to the eventual Brønsted acid.



(8)

Table 1



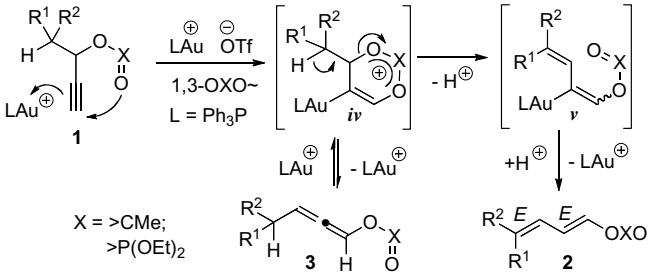
Entry	Substrate		Product		Yield (%)[a]
1		**1a**		**2a**	83
2		**1b**[b]		**2b**	69[c,d]
3		**1c**		**2c**	79
4		**1d**		**2d**	86
5		**1e**[e]		**2e**	75[c,f]
6		**1f**		**2f**	70
7		**1g**		**2g**	82[g]

[a] Isolated yield; 0.5 mmol scale.
[b] 12.5:1 mixture of diastereomers.
[c] 5 mol% of the Au-catalyst was used.
[d] 4.3:1 mixture of (1*E*,3*E*):(1*E*:3*Z*)-dienes.
[e] 1.2:1 mixture of diastereomers.
[f] 1.3:1 mixture of (1*E*,3*E*):(1*E*:3*Z*)-dienes.
[g] 7.5 mol% of the Au-catalyst was used.

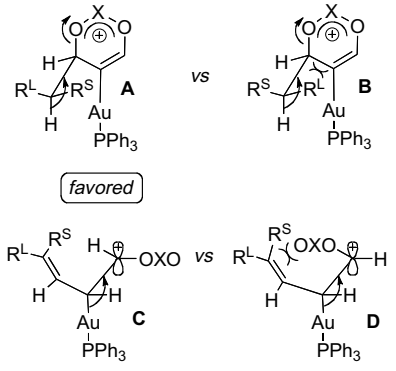
Next, we investigated the scope of this reaction. Thus, isomerization of differently substituted propargylic esters **1a–g** was examined in the presence of $Ph_3PAuOTf$ catalyst (Table 1) [13]. It was found that the cascade transformation of propargylic esters **1a,c,d** possessing various 1,3-migrating groups, such as phosphatyloxy- (entry 1), acyloxy- (entry 3) and pivaloxy- (entry 4), proceeded highly stereoselectively to provide good to high yields of (1*E*,3*E*)-dienes **2a,c,d**, respectively [14]. β-Dialkyl- (entries 5 and 7), alkyl-aryl (entries 2 and 6), as well as β-diaryl- and α-alkyl- (entry 6) substituted propargylic esters, were nearly equally efficient in this transformation, providing corresponding 1,3-dienes **2b,e,f,g** in good to high yields. However, isomerization of phosphates **1b** and **1e**, unsymmetrically substituted at the β-position, proceeded with lower stereoselectivity (entries 2 and 5).

We propose the following mechanism for the cascade transformation of propargyl esters **1** into 1,3-dienes **2** (Scheme 1). The Au(I)-catalyzed 1,3-migration [15] transforms **1** into a cyclic intermediate ***iv*** [1b,3c,5b] which, upon elimination of gold catalyst, furnishes allene intermediate **3**. A direct elimination of the proton from ***iv*** gives a vinyl gold intermediate ***v***, which after the protiodeauration produces 1,3-diene **2** and regenerates the Au(I)-catalyst (Scheme 1).

Exclusive or predominant (1*E*,3*E*)-stereoselectivity of the formation of 1,3-diene products **2**, observed during the Au(I)-catalyzed cascade isomerization of propargylic esters **1**, can be rationalized by the consideration of the stereoelectronic models **A**/**B** and **C**/**D** for the proton elimination and protiodeauration steps, respectively. Accordingly, proton elimination in cyclic ***iv*** occurs through the conformationally more favorable model **A** leading to 3*E*-stereoisomeric ***v***, whereas in the unfavorable model **B** bulkier R_L experiences repulsion with 1,3-dioxenium moiety (Scheme 2). Similarly, 1*E*-configuration in **2** arises from the elimination of Au(I)-catalyst proceeding exclusively via the conformationally preferred model **C** (Scheme 2).



Scheme 1. Mechanistic rationale for Au(I)-catalyzed cascade.



Scheme 2. Stereoelectronic models **A**–**D**.

3. Conclusions

In summary, we developed a mild and stereoselective gold(I)-catalyzed approach toward multisubstituted (1*E*,3*E*)-dienes from propargylic esters which features tandem sequence of 1,3-migration and a proton transfer.

Acknowledgment

The support of the National Institutes of Health (Grant GM-64444) is gratefully acknowledged.

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[13] Representative procedure for the Au(I)-catalyzed isomerization of propargylic esters **1** into (1*E*,3*E*)-dienes **2**: To a foiled 25 ml flask with septa charged with 2.5 mol% of 1:1 mixture of $Au(PPh_3)Cl$ (6.2 mg, 0.0125 mmol) and AgOTf (3.2 mg, 0.0125 mmol) and the 10 ml of anhydrous dichloromethane and stirred for 15 min was then added propargylic phosphate **1a** (141.15 mg, 0.5 mmol) under argon atmosphere and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then filtered through a layer of flash Silica (EtOAc – eluent), the solvents were removed in vacuo, and the residue was purified by column chromatography (EtOAc-Hex: 1:1) to give diethyl (1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl phosphate **2a** (117.4 mg, 83%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 2H), 7.28–7.33 (m, 2H), 7.19–7.24 (m, 1H), 6.83 (dd, J = 11.92, 6.42 Hz, 1H), 6.64 (dd, J = 15.77, 11.00 Hz, 1H), 6.52 (d, J = 15.77 Hz, 1H), 6.21 (t, J = 11.46 Hz, 1H), 4.15–4.24 (m, 4H), 1.37 (td, J = 7.11,

1.01 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7 (d, J_{CP} = 5.5 Hz), 137.1, 132.0, 128.6, 127.5, 126.1, 122.9, 118.0 (d, J_{CP} = 11.1 Hz), 64.6 (d, J_{CP} = 5.5 Hz), 16.1 (d, J_{CP} = 5.5 Hz); HRMS (EI) calcd. for $C_{14}H_{19}O_4P$: 282.10210. Found: 282.10225%.

[14] Unfortunately, employment of internal alkynes possessing alkyl- and aryl substituents in this transformation led to unseparable mixtures of 1,3-dienes in low yields.

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