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Silver(I) catalyzed intermolecular alkene carbo-alkoxylation through cleavage of allylic ether C–O bond

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Introduction

Insertion of the alkene or alkyne groups into the ether's C-O bond is an appealing and useful synthetic tool for the construction of a new ether or vinyl ether structural moieties. In this regard, some transition metals, such as: Pd(0), Au(I) and Pt(II), could be employed to mediate the intra- or intermolecular alkyne's insertion into ether's C-O bond (Scheme 1, Eq. 1) [1-3]. Nevertheless, the similar approach involved the alkene groups seems to be very challenging. To date, only a few examples have ever been reported to realize C–O bond's olefin-insertion reaction [4]. For example, in 2012, Hu and his colleagues reported the gold catalyzed intermolecular carboalkoxylation of alkenes by using acetals as the ether-type substrates (Scheme 1, Eq. 2) [5]. Moreover, intermolecular [3+2] cycloaddition of expoxide with olefin could be carried out through epoxide C-O bond's activation by using Fe(II) or Sc (III) catalysts or under photochemical condition (Scheme 1, Eq. 3) [6]. Despite these achievements, however, acetals and epoxides are not typical ether substrates. Examples of direct intra- or intermolecular olefin-insertion into C-O bond, which involved the other classical types of ethers, are very scarce.

We herein want to report the first example of allylic ether's dimerization reaction through silver catalysis [7], in which, an insertion of the alkene group into allylic ether's C–O bond occurred. In addition, the intermolecular insertion of aromatic ole-fin into allylic ether C–O bond could also be achieved.

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ABSTRACT

All rights reserved. First example of allylic ether's dimerization reaction was developed through olefin's C–O bond insertion via Ag(I) catalysis. Other aromatic olefins, such as styrene and its electro-poor analogues could participate to provide the allylic ether's C–O bond insertion products.

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We recently explored the gold catalyzed enyne cycloisomerization reaction of 1,6-enyne **1a** by using lprAuCl (5 mol%)/AgSbF₆ (10 mol%) as the catalyst combination [8]. Except for the desired major cycloisomerization product **2**, an unexpected dimerization product **3a** could be separated from the reaction mixture in less than 5% yield (Table 1, entry1). According to **3a**'s structure [9], it seems that a double bond rather than a triple bond was activated to insert into the allylic ether bond, wherein, two 1,6-enyne substrates were dimerized to provide **3a** diastereoselectively, with two propargylic units kept intact.

3a's novel structure prompted us to further explore this dimerization reaction. After a series of experiments, we found that silver salt AgSbF₆ could mediate **3a**'s formation. As shown in Table 1, when 1,6-enyne **1a** was treated with 10 mol% of AgSbF₆ in CH₂Cl₂ at rt, dimerization product 3a could be obtained in 41% yield, together with the formation of its inseparable diastereomer 3a' (3a/3a' = 5/1, Table 1, entry 2). Other silver salts, such as: AgNTf, AgOTf, AgBF₄ and AgClO₄, were also tested. But their performances are inferior to that of $AgSbF_6$ (entry 3–6). Then, various solvents, such as: CHCl₃, DCE and CH₃CN, were scrutinized (entry 7–9). It was found that DCE (DCE) was the best reaction media (entry 8), in which, total yields of 3a and 3a' was equal to 46% (3a/3a' = 5/1). Reducing AgSbF₆'s loading to 5 mol% would lead to a relatively lower reaction yield (entry 10). If 10 mol% of AgSbF₆ was added in two batches, the reaction yield could be improved to 54% (entry 11).

With the optimized conditions in hand, we turned to extending the substrate scope by using 10 mol% of $AgSbF_6$ as the catalyst. Dimerization reactions of a series of allylic esters with different

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Scheme 1. Transition metal catalyzed insertion of alkene or alkyne group into C–O bond.

substitution patterns were explored (Table 2). At first, various ether O-substituents, such as: 1,1-diemthyl propargylic group, methyl and ethyl groups, were tested, which readily provided the desired olefin's C-O insertion products. The relatively low yields of **3b** and **3b**' might be owing to the enhanced steric hindrance of the 1,1-diemthyl propargylic unit (compounds 3b and 3b' are inseparable, Table 2). However, to our surprise, the phenol group (Scheme 2, 1i) were not tolerated in this reaction. It seems that only the cinnamyl type ether could participate in the dimerization reaction. As shown in Scheme 2, the allylic methyl ether 1j gave no desired C-O insertion product. Various substituted cinnamyl groups were then examined, in which, the electro deficient groups, such as bromo and chloro substituted cinnamyl ethers (Table 2, **3f/3f**' and **3g/3g**'), performed better than that of their electro-rich counterparts (Table 2, 3e/3e' and 3h/3h'). Furthermore, when the electro-rich 3-(furan-2-yl) allylic ether 1 k (Scheme 2) was treated with AgSbF₆, only a mixture of inseparable products was obtained.

We were wondering if this olefin's insertion into C–O bond reaction could be extending to other aromatic olefins. Thus, a series

Table 1

Silver mediated dimerization of 1,6-enyne 1a.^{a,b,c}



	Cata (mol%)	Solvent	2's Yield	3a & 3a ' Yield (dr) ^{c,d}
1	$IPrAuCl/AgSbF_{6}(5/10)$	CH ₂ Cl ₂	81%	>5%
2	$AgSbF_6$ (10)	CH ₂ Cl ₂	Nd	41% (5/1)
3	AgNTf (10)	CH ₂ Cl ₂	Nd	Trace
4	AgOTf (10)	CH ₂ Cl ₂	Nd	14% (~3/1)
5	$AgBF_4(10)$	CH ₂ Cl ₂	Nd	Trace
6	$AgClO_4$ (10)	CH ₂ Cl ₂	Nd	19% (~5/1)
7	$AgSbF_6(10)$	CHCl ₃	Nd	20%
8	$AgSbF_{6}(10)$	DCE	Nd	46% (5/1)
9	$AgSbF_6$ (10)	CH ₃ CN	Nd	Trace
10	$AgSbF_{6}(5)$	DCE	Nd	33% (5/1)
11 ^e	$AgSbF_{6}(10)$	DCE	Nd	54% (5/1)

^a Unless noted, all reactions were carried out on 0.1 mmol scale in 2 mL anhydrous solvent at rt for 4 h.

^b **3a**, **3a**''s structure only shows relative configuration.

^c Isolated yields.

^d 3a/3a' ratio was determined by ¹H NMR spectral data.

 $^{\rm e}~10$ mol% of AgSbF_6 were added in two batches.

Table 2

Ag(I) mediated dimerization reactions of various allylic ethers.^a



^aUnless noted, all reactions were carried out on 0.1 mmol scale in 2 mL dry DCE at rt for 4 h with the addition of 10 mol% of AgSbF₆ added in two batches (2 h later, the second batch of AgSbF₆ was added 0).

^bIsolated yields.



Scheme 2. Unsuccessful substrates for allylic ether's dimerization reaction.

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Table 3

Ag(I) mediated carbo-oxylation of styrene **4a** with various allylic ethers.^a



^aUnless noted, all reactions were carried out on 0.1 mmol scale (equivalent ratio: 4a/1 = 4/1) in 2 mL dry DCE at rt for 4 h with the addition of 10 mol% of AgSbF₆ added in two batches (2 h later, the second batch of AgSbF6 was added). ^bIsolated yields.

of allylic ethers were evaluated by using styrene as the reaction partner. As shown in Table 3, excess amount of **4a** was added to compete with allylic ether's dimerization reaction. As shown in Table 3, it was found that electro deficient substituents, such as bromo and chloro groups substituted cinnamyl ethers (Table 3, **5c** and **5d**) worked better than their electro-rich analogues (**5b** and **5e**) did in styrene's C–O insertion reactions. A series of ether O-substituents, such as: methyl (Table 3, 5a–e), ethyl (**5f**), propargylic group (**5g**) and benzyl (**5h**) groups, were tolerated (Table 3).

Next, except for styrene **4a**, other aromatic olefins were examined by using methyl *p*-chloro cinnamyl ether **1g** as the reaction partner. As shown in Scheme **3**, the reactions of electro deficient aromatic alkenes, such as: *p*-ClPh (Scheme **3**, **4b**), *p*-FPh (**4c**), *p*-BrPh (**4d**) and *o*-ClPh (**4e**) substituted olefins, went smoothly to provide the desired olefin insertion products in moderate yields (Scheme **3**, **6b-e**), together with the formation of small amount of **1g**'s dimerization products. However, the electro rich aromatic alkene **4f** could not give the insertion product, in which, no dimerization product **3g** and **3g'** were obtained either. This result indicated that **1g**'s dimerization might be inhibited in the presence of **4f**.

In order to elucidate the reaction mechanism, three control experiments were performed. When **1c**'s dimerization reaction was performed in DCE with the addition of 2 equivalent of H_2O , dimerization product **3c** and **3c**' could be synthesized in 40% yield. In addition, a water trapping product **8** was separated in 5% yield



Scheme 3. Ag(I) mediated carbo-oxylation of various aromatic olefins with allylic ether 1g.



Scheme 4. Control experiments of **1c**'s reaction in moisture DCE and allylic alcohol **7**'s reaction.



Fig. 1. X-ray chromatograph for compound 8.

(Scheme 4, Eq. 1), while its *syn*-diastereomer could not be detected. Compound **8**'s structure was determined by its single-crystal X-ray diffraction, in which, a ($1S^*$, $2S^*$) type *trans*- configuration has been confirmed (Fig. 1). When water's amount was improved to 10 equivalence, no desired reaction was observed (Scheme 4, Eq. 1). Trapping the allylic ether **1c** with other nucleophile, such as phenol **9**, could provide *para*-allylic substituted phenol compound **10** in 70% yield (Scheme 4, Eq. 2) [11]. Treating allylic alcohol **7** with AgSbF₆ in DCE gave only trace amount of dimerization products (Scheme 4, Eq. 3).

A plausible simple mechanism was then proposed. As shown in Scheme 5, 1c's dimerization might be started from ether activation by Ag⁺ cation, which provided the allylic cation intermediate I with the removal of AgOMe. Intermediate I reacted with another allylic ether molecule to give intermediate II, which was then trapped by AgOMe to afford the desired dimerization products 3c and 3c'. The *anti*-configuration major product 3c would be thermodynamically favored in this process. Similarly, intermediate II could be trapped by H₂O in the presence of 2 equivalence of water, providing compound 8 in low yield (Scheme 5). Based on Eq. 1's result (Scheme 3), trapping intermediate II with AgOMe should be preferred in the presence of H₂O, possibly because of a certain degree of solvent cage effect [10].

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Scheme 5. Plausible mechanisms for allylic ether's dimerization reaction.

On the other hand, we assumed that the silver catalyst's activity would be inhibited by water, allylic alcohol and electro-rich phenyl groups, which account for the phenomenon of 1i (Scheme 2) and 4f's (scheme 3) unreactivity.

In summary, we have reported Ag(I) catalyzed allylic ether's dimerization reaction through the C-O bond scission and olefin insertion [12]. The insertion reaction could also be extended to styrene and its electro poor analogues. Although there are some limitation upon ether substrates and alkene groups, this is the first example of intermolecular olefin-insertion into the C-O bond, which involved various types of allylic ethers.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2020.151895.

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- [12] General procedure for silver mediated dimerization of allylic ether 1c: To a suspension of 5 mol% of AgSbF6 (3.4 mg) in DCE (2 mL) at rt, was added allylic ether 1c (30 mg, 0.2 mmol). After the reaction mixture was stirred at rt for 2h. the second batch of AgSbF6 (3.4 mg, 5 mol%) was added. The reaction was then kept at rt with TLC monitoring until complete consumption of the starting material. Concentration of the reaction mixture, followed by purification product through flash chromatography (petroleun/EtOAc = 100/1 to 10/1 as the eluent) afforded 3c (15.5 mg) and 3c' (3 mg) as two colorless oil products (63% total yield, 3c/3c, = 5/1). The spectral data of ((4S*,5S*,E)-5-methoxy-4-(methoxymethyl)pent-1-ene-1,5-diyl)dibenzene 3c: 1H NMR (400 MHz, (Inclusion and American Ameri American Ameri American Ameri Americ (m, 3H), 3.22 (s, 3H), 2.30-2.19 (m, 1H), 2.19-2.00 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 140.22, 137.90, 131.68, 128.91, 128.60, 128.36, 127.65, 127.02, 126.08, 83.39, 71.45, 58.96, 57.12, 45.53, 31.16.; HRMS (APCI) Calcd for C20H24O2 (M+H+) 297.1849, Found: 297.1862. The spectral data of ((4S*,5R*, E)-5-methoxy-4-(methoxymethyl)pent-1-ene-1,5-diyl) dibenzene 3c': 1H MR (400 MHz, CDCl3) & 7.40–7.25 (m, 10H), 7.19 (t, J = 7.1 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.23–6.13 (m, 1H), 4.27 (d, J = 6.9 Hz, 1H), 3.32 (dd, J = 9.3, 5.4 Hz, 1H), 3.24 (s, 6H), 3.03 (dd, J = 9.3, 4.9 Hz, 1H), 2.57–2.48 (m, 1H), 2.43– 2.31 (m, 1H), 2.04–1.95 (m, 1H). 13C NMR (101 MHz, CDCl3) δ 140.97, 138.02, 131.52, 129.38, 128.60, 128.37, 127.55, 127.31, 126.97, 126.10, 83.61, 77.48, 77.16, 76.84, 71.74, 58.88, 57.34, 46.32, 30.66. HRMS (APCI) Calcd for C20H24O2 (M+H+) 297.1849, Found: 297.1864.