Gold Catalysis

Gold-Catalyzed Cyclization of Furan-Ynes bearing a Propargyl Carbonate Group: Intramolecular Diels–Alder Reaction with In Situ Generated Allenes

Ning Sun, Xin Xie, Haoyi Chen, and Yuanhong Liu^{*[a]}

Abstract: Gold-catalyzed cyclization of various furan-ynes with a propargyl carbonate or ester moiety results in the formation of a series of polycyclic aromatic ring systems. The reactions can be rationalized through a tandem goldcatalyzed 3,3-rearrangement of the propargyl carboxylate moiety in furan-yne substrates to form an allenic intermediate, which is followed by an intramolecular Diels-Alder reaction of furan and subsequent ring-opening of the oxa-bridged cycloadduct. It was found that the steric and electronic properties of phosphine ligands on the gold catalyst had a significant impact on the reaction outcome. In the case of 1,5-furan-yne, the cleavage of the oxa-bridge in the cycloadduct with concomitant 1,2-migration of the R^1 group occurs to furnish anthracen-1(2H)ones bearing a quaternary carbon center. For 1,4-furanyne, a facile aromatization of the cycloadduct takes place to give 9-oxygenated anthracene derivatives.

Furan rings widely occur as a key structural subunit in numerous natural products and pharmaceuticals.^[1] Substituted furans also serve as synthetic intermediates and building blocks in organic synthesis.^[2] In this regard, the intramolecular Diels-Alder reactions of furan (IMDAF), as the diene component, with a variety of dienophiles, such as activated alkenes, alkynes, or allenes,^[3] have been proved to be a powerful methodology in the synthesis of polycyclic skeletons and in the total synthesis of natural products.^[4] In addition, the resulting oxygen-bridged norbornenes or norbornadienes are valuable precursors for further manipulations,^[5] leading to a wide range of functionalized molecules with biological interest.^[6] Generally, allenes are more reactive than alkenes as dienophiles, however, the utilization of allenes in IMDAF reactions is largely unexplored. Most of studies rely on the reactivity of activated allenes bearing an electron-withdrawing group, which need to be pre-installed by

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multistep synthesis,^[7] or using terminal allenes formed in situ through base-assisted propargyl-allenyl rearrangement.^[8] Therefore, the development of efficient and convenient methods for IMDAF reactions of furans with allenes from easily accessible starting materials with wide structural diversity is highly desirable. During our work on the utilization of the gold-catalyzed 3,3-rearrangement of propargyl carbonates or esters as an efficient tool for the generation of carboxyallenes,^[9] we envisioned that the thus-formed allenes might react with a tethered furan through the Diels-Alder reaction. It was noted that under the gold or platinum catalysis, the furanallenes usually undergo the metal-promoted intramolecular [4+3] cycloaddition by forming a metal-allyl cation intermediate, which often competes with the [4+2] cycloaddition process (Scheme 1). The reaction selectivity depends on the different catalysts, substitution pattern of the substrates, and the reaction conditions. For example, Mascareñas et al. found that the use of PtCl₂/CO or IPrAuCl/AgSbF₆ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) could direct a route of [4+3] cycloaddition.^[10] They also showed in one case that the use of AuCl₃ or AuCl gave the [4+2] cycloadduct predominately at elevated temperature $(110 \degree C)$.^[10a] Toste et al. found that [4+2] and [4+3] cycloadditions of diene-allenes could be controlled by the gold catalyst with different ligands; π -acceptor ligands such as triarylphosphite, favored the formation of a [4+2] cycloadduct.^[11] However, most of the successful substrates used in these studies were diene-allenes, with only limited results derived from furan-allenes. A gold-catalyzed transannular [4+3] cycloaddition of furan-allenes has been explored by Gung et al.,^[12] including the use of propargyl esters as the allene precursors. They also disclosed that the gold-catalyzed intermolecular reaction of terminal propargyl esters with furans proceeded through the [4+3] process. During our studies on gold-catalyzed cyclization of furan-ynes,^[13] we found that ligands played an important role in achieving [4+2] cycloaddition of furans with in situ generated allenes. We now report facile gold-catalyzed cascade reactions of furan-ynes bearing a propargyl carbonate moiety, involving 3,3-rearrangement and IMDAF reactions as the key steps, which provide synthetically valuable anthracen-1(2H)-ones and 9-oxygenated anthracenes with wide functional group tolerance (Scheme 2, Eq. (1) and (2)). The cycloaddition step occurred exclusively by a [4+2] process using bulky biphenyl-di-tert-butyl phosphine derivatives as the ligands. Especially, in the case of 1,5-furanynes, bearing a four-carbon linkage between furan and alkyne moiety, a facile 1,2-migration of the R¹ group occurred to fur-



Scheme 1. Metal-catalyzed [4+3] cycloaddition of furan-allenes.



Scheme 2. Gold-catalyzed [4+2] cycloaddition of furans with in situ generated allenes.

nish the anthracenones containing a quaternary carbon (Scheme 2, eq 1).

Recently, we developed various gold-catalyzed intramolecular cyclizations of benzene-tethered furan-ynes, initiated by attack of the furan on the gold-activated alkyne, followed by furan ring-opening.^[13] These initial results make the current target 3,3-rearrangement/IMDAF reactions with high selectivity a challenging task. To initiate an allene formation, 3,3-rearrangement of the propargyl carbonate moiety in designed substrates 1 should occur more rapidly than the furan-yne cyclization.^[14] Here, we expected that the desired transformation might be achieved through variation of the different ligands on gold. To test the feasibility of our hypothesis, we initially examined the gold-catalyzed reactions of 1,5-furan-yne 1a bearing a phenyl substituent at the alkyne terminus; the results are shown in Table 1. Treatment of 1 a in DCE (1,2-dichloroethane) with cationic gold(I) complex PPh₃AuSbF₆, generated in situ, afforded only a complex reaction mixture (Table 1, entry 1). To our delight, the use of a gold catalyst with an N-heterocyclic carbene (NHC) ligand, after stirring the reaction mixture in DCE at 50°C for 2 h, provided the desired anthracen-1-(2H)-one 2a in 56% yield, along with 7% of byproduct anthracene ${\bf 3a}$ (entry 2). The structure of 2a was unambiguously confirmed by X-ray crystallography.^[15] The results indicated that an interesting 1,2-migration of the phenyl group occurred during the reaction process, resulting in the assembly of a quaternary carbon center adjacent to a carbonyl functionality in 2a. Decomposition of the substrate was observed only in the presence of AgSbF₆ (entry 3). When [JohnphosAu(MeCN)]SbF₆ (catalyst A) was used (Johnphos = (2-biphenyl)di-tert-butylphosphine), the yield of 2a increased to 67%, along with 9% of 3a (entry 4). Gratifyingly, it was found that gold catalyst B with tBuXphos (2-di-tert-butylphosphino-2',4',6'-triisopropylbiphenyl) as the ligand was more efficient for this transformation, leading to 84% yield of 2a, whereas the formation of 3a was completely inhibited (entry 5). Gold complexes possessing other bulky phosphine ligands such as Sphos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl, catalyst C) catalyzed this reaction less efficiently, leading to 2a in 42% yield (entry 6). Interestingly, the use of (Me)₄tBuXphos as the ligand (catalyst D) resulted in the formation of a diastereomeric mixture of [4+2] cycloadducts 4a and 4a' in high yield (entry 7). These results indicated that the steric and electronic properties of phosphine ligands on gold catalysts had a significant impact on the reaction outcome. When the reaction was run at room temperature using catalyst B, the cycloadduct 4 could also be observed, along with 27% of 2a (entry 9). This suggests that 4 might be the intermediate leading to product 2. Decreasing the amount of catalyst B to 2 mol% gave 2a in a lower yield of 59% (entry 10). Changing the solvent to toluene or THF afforded 2a also in lower yields of 49 or 33% (entries 11, 12, respectively). We then investigated the effect of the protecting groups on this reaction. Acetyl- (Ac), pivaloyl- (Piv), or benzoylprotected (Bz) substrates 5a-c, respectively, resulted in remarkable decreases in product yields (24-46%), along with the formation of several byproducts (entries 13-15). These results reveal that the nature of the protecting groups on the alcohol is also crucial for successful transformation. In this reaction, a carbonate substrate is converted into 2a more efficiently than those of esters, possibly due to the enhanced stability of the carboxyallene intermediate for the carbonate cases.

Next, the scope of the gold-catalyzed cascade reaction was evaluated under the conditions shown in Table 1, entry 5 (conditions a); the results are shown in Table 2. We first investigated the electronic effect of the aryl substituents on the alkyne terminus. We were pleased to find that a series of electronwithdrawing groups substituted on the aryl alkynes such as p-F, p-Cl, p-CF₃, and p-CO₂Et underwent the cyclization smoothly to provide the corresponding anthracenones 2b, c, e, f in 64-86% yields in short reaction times. However, when aryl alkynes bearing substituents such as p-Br or p-OMe were employed, the desired products were obtained only in low yields under conditions a, possibly due to the rapid decomposition of the starting materials. We then made efforts to re-optimize the reaction conditions for those particular alkynes. Gratifyingly, we found that simply changing the counterion from SbF₆⁻ to OTf⁻ (Tf = trifluoromethanesulfonyl) in the gold catalyst led to 70% yield of 2g bearing a p-OMe-substituted aryl group (conditions b, 5 mol % tBuXphosAuCl/AgOTf). Under these conditions, p-Br-substituted 1d afforded 2d in a high yield of 88%. Electron-rich aryl alkynes with p-Me, p-tBu, 3-OMe, or 3,4,5-(OMe)₃ substituents were also well suited under these conditions, furnishing 2h-k in 42-78% yields. A thienyl group was well tolerated under conditions b, leading to the desired product 21 in 73% yield. The use of alkynes with an alkyl substituent such as nBu resulted in a complex mixture of products, in DCE. In contrast, when the reaction was carried out in THF, this substrate isomerized rapidly within 30 minutes at room temperature to give allenyl carbonate 6m in 69% yield. A cyclopropyl-substituted alkyne also afforded allene product 6n in 79% yield in THF. However, extending the reaction time formed a complex reaction mixture, and the desired anthracen-1(2H)-ones were not observed in these cases. Cyclization of substrate 1o with



Table 1. Optimization studies for the formation of 2a.								
		Ph Ph Me	5 mol% catalyst solvent	O Ph Me +	Ph Me 3a			
			MeO ₂ C	A A A A A A A A A A A A A A A A A A A	AleO ₂ CO Ph Me 4a'			
		$(Bu \xrightarrow{fBu}_{p^{-}Au = NCMe} R^{1} \land R^{1} \land R^{1}$	Cy P-Au-NCMe Me MeO Me	tBu [†] St P-Au−NCMe iPr iPr iPr iPr iPr	$r = \frac{1}{Cl}$			
		A : R ¹ = H B : R ¹ = <i>i</i> Pr	с	D	E			
							Yield [%] ^[a]	
Entry	Substrate	Catalyst	Solvent	<i>T</i> [°C]	<i>t</i> [h]	2a	3 a	4 a/4 a′
1	$R = CO_2 Me(1 a)$	PPh ₃ AuCl/AgSbF ₆	DCE	RT	2	_ ^[b]	_	-
2	1a	IPrAuCl/AgSbF ₆	DCE	50	2	56	7	-
3	1a	AgSbF ₆	DCE	RT	2	_ ^[b]	-	-
4	1a	Α	DCE	50	4	67	9	-
5	1a	В	DCE	50	2	84 ^[c]	-	-
6	1a	c	DCE	50	2	42	7	-
7	1a	D	DCE	50	6	-	-	47/44
8	1a	E	DCE	50	6	-	-	10/14
9	1a	В	DCE	RT	12	27	-	13/20
10	1a	В	DCE	50	5	59 ^[d]	-	-
11	1 a	В	toluene	50	3	49	-	-
12	1a	В	THF	50	3	33	-	-
13	R = Ac (5 a)	В	DCE	50	5	24	-	-
14	R = Piv (5 b)	В	DCE	50	3	44	-	-
15	R = Bz (5 c)	В	DCE	50	3	46	-	-
[a] NMR yields determined by ¹ H NMR using CH_2Br_2 as an internal standard. [b] A complex reaction mixture was observed. [c] Yield of isolated product was 80%. [d] 2 mol% of catalyst B was used.								

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a C-5 unsubstituted furan ring occurred smoothly to give 1phenylanthracen-2-ol (**7**) in 63% yield under conditions b. The structure of **7** was confirmed by the X-ray crystallography analysis of its OAc derivative,^[15] in which no 1,2-phenyl migration occurred.

We propose the following reaction mechanism for the above-mentioned transformations (Scheme 3). Initially, gold-catalyzed 3,3-rearrangement of the propargyl carbonate moiety affords carboxyallene intermediate **6**. This is followed by IMDAF reaction to give an oxa-bicyclic alkene intermediate **4**. Then, gold-assisted cleavage of the oxa-bridge in cycload-duct **4** takes place to give alcohol intermediate **9**.^[14] Subsequent 1,2-migration of the R¹ group, followed by reaction of the resulting oxocarbenium ion **11** with a LAuOH (L=ligand) species furnishes the anthracenone products **2**.^[16] In the case of **1 o** (R²=H), elimination of the carbonate group occurred to afford **7**, due to the ease of aromatization.

To understand the reaction mechanism, we carried out the following control experiments (Scheme 4). Treatment of cycloadduct 4a or 4a' in the presence of gold catalyst **B** in DCE afforded ring-opened product 2a in high yields. However, without gold catalyst, no reaction occurred. It was therefore concluded that ring opening of the oxa-bridge in intermediate 4proceeded with the assistance of Lewis acid.



Scheme 3. Possible reaction mechanism for the formation of anthracenones 2.

After the success of the transformation of 1,5-furan-ynes 1, we next attempted to extend this cyclization reaction to 1,4-furan-yne substrates 12 with a three-carbon linkage between the furan and alkyne moieties. A brief optimization of reaction conditions was carried out, the results of which are shown in Table 3. It turned out that the use of gold catalysts with bulky phosphine ligands afforded the desired 9-oxygenated anthracenes 13 a in generally good to high yields, and the best result was achieved using [tBuXphosAu(MeCN)]SbF₆ (catalyst **B**) (Table 3, entries 1–4). When frequently used gold complexes such as PPh₃AuNTf₂ or PPh₃AuSbF₆ were employed as the catalyst, only low product yields of 37 and 10%, respectively, were

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Scheme 4. Control experiments.

observed (Table 3, entries 5, 6). The scope of this reaction is shown in Table 4. In most cases, the 3,3-rearrangement/cycloaddition cascade of substrates 12 proceeded quite efficiently, catalyzed by 5 mol% of catalyst ${\bf B}$ (DCE, 50 $^{\circ}{\rm C},$ 1–3 h), leading to 13 in good to excellent yields. In the present reaction, both electron-withdrawing [p-Cl, p-CF₃, p-CN, o-Br, o-F, 3,5-di-Cl] and electron-donating [p-Me, 3-OMe, 3,5-di(OMe), 3,4,5-tri(OMe)] aryl substituents were well-tolerated during the process, furnishing the corresponding anthracene derivatives 13b-k in 50-96% yields. In particular, sterically encumbered o-Br-substituted substrate 12 f was smoothly converted into the corresponding 13 f in a high yield of 89%. When a substrate bearing an alkyl group, such as a *n*-butyl group at the propargylic position (121), was employed, a completely different product of naphthalene 14 with a cis-enone moiety was obtained in 70% yield. In this case, a competitive gold-catalyzed cyclization of furan-ynes with ring-opening of the furan moiety occurred, similar to that of gold-catalyzed cycloisomerization of TBS-protected (o-alkynyl)phenyl 2-furylcarbinols leading to protected 1-naphthols reported by us.^[13d] This result, in which **14** was obtained, indicated that the furan-yne cyclization occurred more rapidly than 3,3-rearrangement of the propargyl carbonate moiety. In addition to the carbonate substrates, propargyl acetate or benzoate were also well suited for this reaction, providing **13 m** and **13 n** in 91% and 94% yields, respectively.



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We propose the following reaction mechanism for the formation of products **13** (Scheme 5). In the first step, an efficient gold-catalyzed 3,3-rearrangement occurs to afford the carboxyallene intermediate **15**. This is followed by the IMDAF reaction to give an oxa-bicyclic intermediate **16**, ring-opening of **16**, and aromatization, which delivers the anthracene products **13**.

The synthetic utility of these functionalized anthracene products was also briefly investigated (Scheme 6). Interestingly, in the presence of ceric ammonium nitrate (CAN), a deprotection followed by oxidation of **13m** occurred smoothly in air, leading to anthraquinone **17** and its dimer **18** in 61% and 30% yields, respectively. To our surprise, when the reaction was carried out in CH₃CN, **18** was formed as the only product in 95% yield. Anthraquinones are an important class of naturally occurring substances,^[17] and they are also known as efficient building blocks in the synthesis of polysubstituted acenes for usage in organic functional materials.^[18] Thus, our method provides a facile route for these compounds. In conclusion, we have developed an efficient and cascade approach for IMDAF reactions with allenes. The allene moiety can be constructed conveniently by a gold-catalyzed 3,3-rearrangement of the propargyl carbonates or in some cases, esters, which undergo subsequent IMDAF reaction followed by ring-opening of the oxa-bridged cycloadduct to afford polycyclic aromatic skeletons. In the case of 1,5-furan-yne, the cleav-



Scheme 5. Possible reaction mechanism for the formation of anthracenes 13.

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Scheme 6. Transformation of anthracene 13 m (d.r. = diastereomeric ratio).

age of the oxa-bridge in the cycloadduct with concomitant 1,2-migration of an aryl group occurs to furnish anthracen-1(2H)-ones bearing a quaternary carbon center. In the case of 1,4-furan-yne, a facile aromatization of the cycloadduct takes place to give 9-oxygenated anthracene derivatives. Further applications of this cascade reaction to the synthesis of diverse complex molecules are currently under way.

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Keywords: allenes · diels-alder reaction · furans · gold catalysis · propargyl carbonates

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- [16] The unusual formation of 3a shown in Table 1, entries 2, 4, and 6 might be rationalized by following the tandem reaction: Initially, a propargyl carbocation is formed by decarboxylation,^[9a] which may equilibrate with the allenyl carbocation. A hydride transfer from AuOMe produces the allene, which undergoes a Diels-Alder reaction followed by ringopening, and aromatization to afford 3a.



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The power of gold: Gold-catalyzed cyclization of various furan-ynes with a propargyl carbonate or ester moiety results in the formation of a series of polycyclic aromatic ring systems. The reaction consists of a tandem gold-catalyzed 3,3-rearrangement of the proparg-yl carboxylate in the furan-ynes to form

an allenic intermediate, followed by an intramolecular Diels–Alder reaction of furan and subsequent ring-opening of the oxa-bridged cycloadduct. The steric and electronic properties of phosphine ligands on the gold catalyst had a significant impact on the reaction outcome.

Gold Catalysis

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Gold-Catalyzed Cyclization of Furan-Ynes bearing a Propargyl Carbonate Group: Intramolecular Diels-Alder Reaction with In Situ Generated Allenes