

Silver(I)-Catalyzed Oxidative Intramolecular Cyclopropanation: Access to Complex Tricyclo[3.3.1.0]nonanediones via Semipinacol-Type Rearrangement

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oxidant. The transformation involves the formation of a perchloryloxy vinyl-silver species, which then proceeds through either intramolecular conjugate addition or an α -oxo silver carbene pathway to yield cyclopropane fused tricyclic enones with high



diastereoselectivity. In the case of C-tethered cyclohexadienones, the reaction proceeds further via acid mediated semipinacol-type rearrangement to give complex and highly strained tricyclo [3.3.1.0] nonanediones. This cascade annulation has wide functionalgroup tolerance and broad substrate scope. Late-stage functionalization of estrone was also demonstrated with excellent diastereoselectivity.

evelopment of new strategies to generate the cyclopropanes have received considerable attention from the synthetic organic chemists due to their presence in a wide range of natural products, drugs, and agrochemicals.¹ In addition, these highly strained (~ 27 kcal/mol) threemembered rings have several potential applications through ring-opening reactions to construct complex molecules.² Consequently, numerous strategies have been developed to generate cyclopropanes, built around a variety of ylides³ and stabilized carbanions,⁴ as a versatile methylene source. Another attractive approach is the decomposition of relatively stable α diazo carbonyl compounds via late transition metal carbenes.⁵ However, diazo compounds are difficult to handle on large scale and prepared from carbonyl precursors with energetic reagents in multiple steps, leading to limited synthetic potential.

Significantly, over the past few years, alkynes were explored as an alternative source to generate α -oxo metal carbenes.⁶ Several elegant methods have been developed based on intramolecular oxidation where required oxidant should be tethered to the alkyne with optimal distance.⁷ In 2010, Liming Zhang and co-workers disclosed the generation of highly electrophilic α -oxo gold carbenes using pyridine N-oxide as an external oxidant for the first time⁸ exhibiting the versatile reactivity en route to cylopropanation⁹ of tethered or external alkenes including various other transformations¹⁰ (Scheme 1a).

Previously, Sanford and others elegantly demonstrated the Pd(II/IV)-catalyzed α -oxo cyclopropanation of envnes in the presence of PhI(OAc)₂ as an oxidizing agent (Scheme 1b).¹¹ Silver (Ag) is more abundant and a less expensive precious

Scheme 1. Previous and Present Approaches on Metal-Catalyzed α -Oxo Cyclopropanations



-oxo silver carben

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metal, and its salts are also excellent π -activators of carbon– carbon triple bonds. However, silver-catalyzed syntheses of cyclopropanes are more common in diazo chemistry¹² and are rarely reported from alkynes via intramolecular oxidation.¹³ Surprisingly, silver-catalyzed cyclopropanation from the carbon–carbon triple bond with an external oxidant has not been explored to date. Herein, we report the first Ag(I)catalyzed oxidative cyclopropanation of cyclohexadienonecontaining 1,6-enynes using an external oxidant with high yields and excellent diastereoselectivities (Scheme 1c).

Desymmetrization of prochiral cyclohexadienones is a powerful and straightforward strategy for the rapid construction of highly functionalized molecules. Over the past decade, our group¹⁴ and others¹⁵ have developed a wide range of stereoselective desymmetrization methods utilizing transition-metal catalysis. To further extend the utility of these unique substrates, we envisioned that the silver-catalyzed annulation of prochiral alkyne-tethered cyclohexadienones could lead to cyclopropane fused cyclohexenones (Scheme 1c). The reaction might proceed through either formation of Ag-enolate via intramolecular conjugate addition of a vinyl–Ag complex (Path A) or α -oxo silver carbene intermediate via back-donation from the metal center in the vinyl–Ag complex (Path B). The regioselective oxidation of activated triple bond is a major challenge in this particular process.

We initiated the study with cyclohexadienone **1a** as a model substrate and investigated the anticipated intramolecular cyclopropanation in the presence of 10 mol % AgClO₄ in CH_2Cl_2 at 50 °C. Here, counteranion ClO_4^- acts as an oxidant to give the required product **2a** in 10% yield with exclusive diastereoselectivity (Table 1, entry 1). Later, the catalyst loading was increased gradually and provided the highest yield of **2a** (78%) with 100 mol % of AgClO₄ (entries 2–4). The study clearly indicated that the reaction medium should have an external oxidant in the equimolar ratio to improve the yield.

Table 1. Optimization of Reaction Conditions^{*a,b*}



^{*a*}Reaction conditions: **1a** (1 equiv) in CH₂Cl₂ (0.1 M) at 50 °C. ^{*b*}Used ~70% aqueous HClO₄ solution. ^{*c*}Isolated yields. ^{*d*}Reaction yield (32%) at room temperature. ^{*c*}Starting material was decomposed.

Remarkably, the reaction in the presence of 10 mol % catalyst with 2 equiv of perchloric acid proceeds rapidly $(\sim 1 h)$ to furnish the annulation product 2a in 22% yield (entry 5). To the best of our knowledge, simple HClO₄ was used as the oxidizing agent in the transition-metal catalyzed cyclopropanation for the first time. Next, various silver catalysts were examined (see Supporting Information) and AgNO₃ worked rationally well compared to other silver salts, affording the desired product 2a in 36% yield (entry 6). Increasing AgNO₃ loading or decreasing HClO₄ substantially increased the reaction yield up to 76% (entries 7 and 8). Lower or higher reaction temperatures proved to be inferior in terms of reaction yields. Other transition-metal catalysts under these conditions gave moderate yields (entries 9-12). The control reaction without catalyst loading did not produce the required product 2a, and starting material was decomposed (entry 13). Overall, the reaction progressed very efficiently in the presence of 10 mol % of AgNO₃ and 1 equiv of HClO₄ at 50 °C (entry 8). The structure and relative stereochemistry of compound 2a were unambiguously determined by single crystal X-ray analysis.

Initially, we diversified the scope of aryl- and alkyl substituted alkyne-tethered cyclohexadienones under optimized reaction conditions (Scheme 2). Despite a bulky



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^{*a*}Reaction conditions: 1 (0.3 mmol), AgNO₃ (5.1 mg, 10 mol %) in CH_2Cl_2 (0.1 M), $HClO_4$ (26 μ L, ~70% aq. solution). ^{*b*}Isolated yields. ^{*c*}The diastereomeric ratio (dr) was assigned by ¹H NMR analysis.

substituent at the prochiral quaternary center, the reactions still proceeded well with good yields and exclusive diastereoselectivity (entries 2a-2e). In the case of the *sec*-butyl substituent, the corresponding product 2d was furnished as a 1:1 ratio of diastereomers. Later, the substrate scope was examined with various aryl substituents on the propargylic group of cyclohexadienones 1. All aryl substrates gave moderate to good yields (2f-2t, 36-81% yield). In particular, electron-donating substituents and sterically hindered *ortho*- substituents on the aryl ring afforded annulation products in slightly lower yields. It is worth mentioning that methylsubstituted alkyne, also well tolerated in the reaction, gave required product 2u in acceptable yield. Interestingly, the *trans*-4-amylcyclohexyl substituent at the substrate's prochiral quaternary carbon center proceeded smoothly to give desired product 2v in 61% yield with a >30:1 ratio of diastereose-lectivity. To our delight, *N*-tethered cyclohexadienones also well tolerated in this transformation to afford corresponding tricyclic products 2w and 2x in excellent yields. Unfortunately, we were unable to expand the substrate scope with terminal alkyne-tethered cyclohexadienones, presumably due to the formation of the silver-acetylide intermediate to allow the complex reaction mixture.

On the basis of the above results, we evaluated the scope of intramolecular cyclopropanation with various 1,3-diyne-tethered cyclohexadienones 3 (Scheme 3). The annulation with all





^aReaction conditions same as in Scheme 2. ^bIsolated yields.

aryl and heteroaryl substituted 1,3-diynes under standard reaction conditions proceeded smoothly in good yield with complete diastereoselectivity (entries 4a-4e). Here, selective π -bond activation of alkyne proximal to the cyclohexadienone ring with Ag(I)-catalyst followed by perchloryloxy vinyl-silver intermediate formation allowed facile cyclopropanation. This specific regioselectivity observed is presumably due to the π bond chelation between the Ag-complex and cyclohexadienone.^{16,14c} The substrates having cyclohexene, cyclopropane, and various alkyl chains on diyne showed a similar reactivity to give corresponding fused cyclopropanes 4f-4k in 61-70% yield. Interestingly, the reaction with a complex natural product linked cyclohexadienone also afforded the desired product 41 in acceptable yield. For N-tethered 1,3-diynes, the reaction was well tolerated with phenyl, cyclohexenyl, and cyclopropyl substituents to give the cyclization products in good yields (entries 4m-4o).

Next, we sought to examine the scope of C-tethered cyclohexadienones in the Ag-catalyzed oxidative cyclization reaction. Interestingly, this transformation led to the discovery of highly strained complex tricyclo[3.3.1.0]nonanedione products via semipinacol-type rearrangement¹⁷ (Scheme 4). When **5a** was treated under standard reaction conditions, the reaction proceeded smoothly within 1 h, affording the bridged

Scheme 4. Semipinacol-Type Rearrangement of C-Tethered Cyclohexadienone



tricyclononanedione 6a in 58% yield. It is worth mentioning that the quenching of reaction within 10 min allowed us to isolate key cyclopropane intermediate A in 32% yield (for R =Me). This clearly indicates that the oxidative cyclopropanation indeed took place initially to give fused tricyclic intermediate A and subsequent acid mediated semipinacol-type rearrangement followed by hydrolysis affording highly complex product 6a. The C-tethered cyclopropane intermediate A is more strained as compared to O-tethered and N-tethered cyclopropanes (2 or 4) due to the presence of the Thorpe–Ingold effect.¹⁸ At the same time, acid-mediated enhancement of enone electrophilicity in intermediate A facilitates the regioselective 1,2migration of nucleophilic carbon center via Michael addition providing bridged tricycle 6a. Subsequently, the reactivity of other alkoxy substrates 5a' and 5a" were also investigated, wherein ethoxy-tethered cyclohexadienone 5a' gave a higher yield (64%) than others.

The generality of the semipinacol-type rearrangement reaction was investigated using various C-tethered cyclohexadienones under standard reaction conditions (Scheme 5). In all cases, a range of aryl-substituted alkynes varying steric and electronic properties were well tolerated to furnish the desired tricyclononanediones (6a-6i) in good yields. The structure and relative stereochemistry of product 6a were determined by an X-ray crystallographic analysis. Furthermore, naphthyl, phenanthryl, and fluorenyl derivatives (6f, 6g, and 6h) were found to be similar in reactivity like other aryl substrates. It was intriguing to find thiophene substituted Ctethered alkyne gave the highest yield (6i). Next, the reactivity of 1,3-diyne-tethered cyclohexadienones in the oxidative rearrangement reaction was examined. Gratifyingly, aryl, alkenyl, and alkyl substituted 1,3-diynes were suitable substrates for this transformation, providing the corresponding bridged tricyclic products (6j-6o) in synthetically acceptable vields.

Encouraged by these observations, we proceed to utilize intramolecular oxidative cyclopropanation for late-stage functionalization of estrone (Scheme 6a). Under standard reaction conditions, estrone derivatives 7a and 7b (synthesized from estrone in two steps)¹⁹ afforded corresponding optically active products 8a and 8b, with excellent diastereoselectivity. Next, silyl ether 9 was treated under optimized conditions to afford fused tetracycle 10 in 56% yield as single isomer via a cyclopropanation/desilylation/*oxa*-Michael addition sequence (Scheme 6b). To gain further insight into the mechanism of cyclopropanation reaction, we subsequently designed an experiment using $H_2^{18}O$ (9 equiv) under standard conditions which furnished 2a without the ¹⁸O incorporation, presumably



Scheme 5. Substrate Scope for Semipinacol-Type Rearrangement a,b

^{*a*}Reaction conditions: **3** (0.26 mmol, 1 equiv), AgNO₃ (4.4 mg, 10 mol %) in CH₂Cl₂ (0.1 M), HClO₄ (23 μ L, ~70% aq. solution; 1 equiv), at 50 °C for 1 h. ^{*b*}Isolated yields.

Scheme 6. Synthetic Utility and Labelling Study



due to interference of H₂O from a 70% aqueous solution of $HClO_4$ (Scheme 3c). To avoid the influence of H₂O, we conducted the reaction in the presence of AgClO₄ (1 equiv) and H₂¹⁸O (9 equiv) in anhydrous CH₂Cl₂ solvent which afforded a mixture of 2a/2a-¹⁸O in 48% yield. The ESI-HRMS analysis revealed that the formation of both ¹⁶O and ¹⁸O labeled products (see Supporting Information) and this experiment suggests that the oxidation probably stems from the ClO_4^- counterion.²⁰

Based on these results and previous reports,^{11,13} we proposed two possible reaction pathways in Scheme 7.

Scheme 7. Plausible Mechanism



Initially, a highly alkynophilic Ag(I)-catalyst coordinate with a triple bond to form an (η^2 -alkyne)silver complex I, followed by intermolecular oxidation with a perchlorate anion, produces vinyl-Ag intermediate II. This intermediate might react in two different pathways (A and B) to give the required product 2a. In path A, the vinyl-Ag intermediate II could undergo intramolecular Michael addition to give bicyclic silver-enolate III and subsequent intramolecular attack on electron-poor vinyl perchlorate gives cyclopropane fused enone 2a by the elimination of the ClO₃⁻ anion.¹¹ On the other hand (Path B), back-donation from the metal center in intermediate II would eliminate the ClO₃⁻ anion to give α -oxo silver carbene IV, which reacts consecutively with proximal electron-deficient enone to produce corresponding product 2a and regenerate the Ag(I) catalyst.^{13a}

In conclusion, we have developed a new silver(I)-catalyzed oxidative annulation for the stereoselective desymmetrization of prochiral cyclohexadienones, leading to fused α -keto cyclopropanes. Simple perchloric acid is found to be a suitable oxidizing agent for the first time in the transition-metal catalyzed cyclopropanation. The reaction has been accomplished through the formation of a selective perchloryloxy vinyl-silver intermediate to give cyclopropane-fused enone via either intramolecular conjugate addition or an α -oxo silver carbene pathway. For C-tethered substrates, acidic reaction conditions facilitated semipinacol-type rearrangement to give highly strained and complex tricyclo[3.3.1.0]nonanediones with complete diastereoselectivity. We found that the broad range of substrates including alkyl, aryl substituted alkynes and 1,3-diynes are well tolerated in this transformation. Additionally, the methodology allowed the late-stage functionalization of complex natural product estrone with excellent diastereoselectivity. The mechanistic as well as enantioselective studies of this strategy are in progress and will be reported in due course.

ASSOCIATED CONTENT Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02555.

Experimental procedures, characterization details, ¹H and ¹³C NMR spectra of new compounds, and X-ray

crystallographic data for representative compounds (PDF) $% \left(PDF\right) =\left(1-2\right) \left(1$

Accession Codes

CCDC 1983894 and 1983896 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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