

A General Synthesis of Ynones from Aldehydes via Oxidative C–C bond Cleavage under Aerobic Conditions

Zhaofeng Wang, Li Li, and Yong Huang*

Key Laboratory of Chemical Genomics, School of Chemical Biology and Biotechnology, Peking University, Shenzhen Graduate School, Shenzhen, 518055, China

S Supporting Information

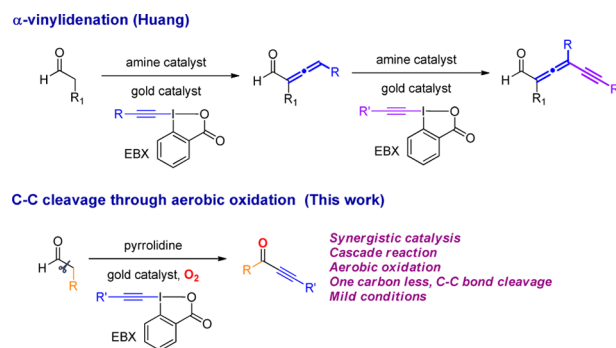
ABSTRACT: We describe a direct synthesis of various ynones from readily available aldehydes and hypervalent alkynyl iodides. In this method, a gold catalyst and a secondary amine work synergistically to produce the trisubstituted allenyl aldehyde, which can be converted to the desired ynone through an *in situ* C–C bond oxidative cleavage using molecular oxygen.

The combination of a metal and an organocatalyst in a single pot is a powerful strategy to accomplish previously unattainable chemical transformations.¹ The merge of metal catalyzed aerobic oxidation and small organic molecule catalyzed C–C bond formation reactions represents a unique and refreshing approach to access synthetically valuable intermediates. Yet, successful metal-organocatalysis synergy and types of competent reactions remain scarce despite the enormous advances enjoyed by both metal catalysis and organocatalysis alone. In particular, catalytic C–C bond cleavage represents a major challenge for the synergistic catalysis. Although metal catalyzed C–C bond cleavage has been studied extensively using transition metals, the reaction substrates often require additional synthetic efforts.² *In situ* assembly of appropriate functionalities (ready for C–C bond cleavage using metal catalysts) via organocatalysis enables direct employment of commercially cheap feedstock for such reactions.

Alkynyl carbonyl compounds, especially ynones, are abundant structural motifs in natural products. They are often employed as a key template for rapid structural proliferation toward sophisticated synthetic targets.³ The direct attachment of a carbonyl to an acetylene moiety offers numerous synthetic outlets for structure diversification. For example, ynones are particularly attractive as precursors to various heterocycles, such as pyrroles,⁴ furans,⁵ furanones,⁶ pyrazoles,⁷ isoxazoles,⁸ pyrimidines,⁹ flavones,¹⁰ quinolones,¹¹ etc. Considerable efforts have been made to access ynones using various synthetic approaches.^{12–16} In most cases, both reaction partners need to be preactivated or an additional step was required. More recently, method development for the synthesis of ynones has been focused on mild conditions, wide functional group tolerance, readily available starting materials, and practical convenience. Müller et al. reported a series of Sonogashira couplings reactions between acyl chlorides (and aryl halides in the presence of CO) and terminal alkynes utilizing Pd–Cu catalysts.^{9,17} Bolshan et al. reported a metal-free synthesis of ynones from acyl chlorides and potassium alkynyltrifluoroborate salts.¹⁸ Hashmi et al. reported a

gold catalyzed dehydrogenative Meyer–Schuster-like rearrangement to generate ynones.¹⁹ Despite these contributions to ynone synthesis, a mild, practical method to prepare ynones using readily available materials is highly desirable. Toward this goal, we report our recent progress on direct synthesis of ynones from aldehydes using synergistic catalysis (Scheme 1).

Scheme 1. α -Functionalization of Aldehydes Using Amine/Gold Synergistic Catalysis



Recently we reported the first direct α -vinyldienation of aldehydes to access trisubstituted allenyl aldehydes using synergistic catalysis combining a gold catalyst and a secondary amine.²⁰ Subsequently, we found that the α -allenyl aldehyde could further react with a secondary amine to generate the corresponding ynenamine intermediate, which was reactive toward various electrophiles. We wondered whether this highly electrophilic species would be sensitive to *in situ* oxidation using molecular oxygen to yield an oxidation product. The trisubstituted allenyl aldehyde was stirred with 1 equiv of pyrrolidine and a metal catalyst under an oxygen balloon. Gratifyingly, AuCl₃ was found to promote a clean aerobic oxidation reaction to give an ynone product **2a** in 88% yield.²¹ This compound contained one less carbon than the starting materials combined, indicating a C–C bond cleavage process.

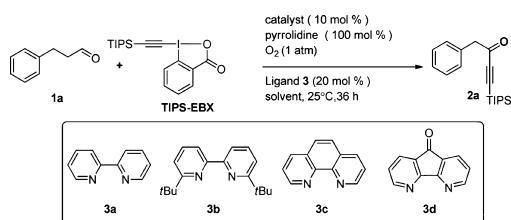
Encouraged by this result, we initiated an attempt to synthesize ynones directly from aldehydes in a one-pot manner. The reaction conditions survey was carried out by treating a mixture of aldehyde **1a** (1 equiv), pyrrolidine (1 equiv), and 1-[(triisopropylsilyl)-ethynyl]-1,2-benziodoxol-3(1H)-one (TIPS-EBX, 1.2 equiv)²² in the presence of a metal catalyst under

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an oxygen balloon at rt (Table 1). Only gold promoted this aerobic C–C bond cleavage reaction. No ynone product **2a** was

Table 1. Conditions Survey for the Direct Conversion of Aldehydes to Yrones^a



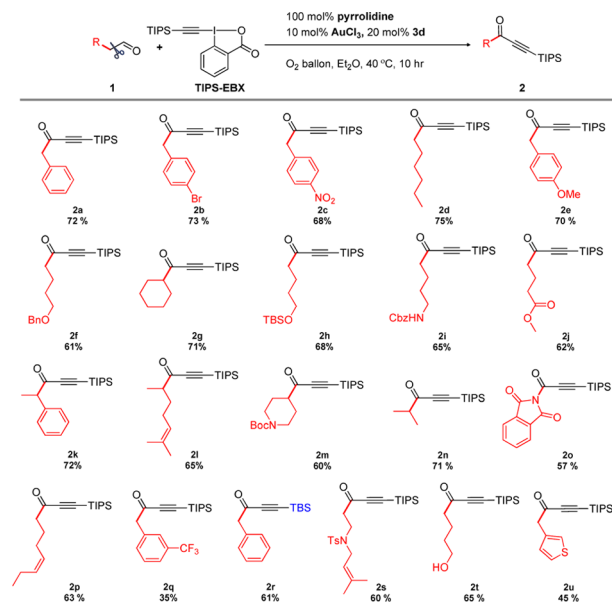
entry	solvent	catalyst	ligand	yield (%) ^b
1	toluene	Cu	none	0
2	toluene	Ag	none	0
3	toluene	Fe	none	0
4	toluene	AuCl	none	trace
5	toluene	AuCl ₃	none	13
6	toluene	AuCl	3a	27
7	toluene	AuCl ₃	3a	41
8	Et ₂ O	AuCl	3a	32
9	Et ₂ O	AuCl ₃	3a	53
10	Et ₂ O	AuCl ₃	3b	trace
11	Et ₂ O	AuCl ₃	3c	trace
12	Et ₂ O	AuCl ₃	3d	68
13 ^c	Et ₂ O	AuCl ₃	3d	81
14	DMF	AuCl ₃	3d	trace
15	THF	AuCl ₃	3d	32
16	DME	AuCl ₃	3d	21
17	EtOH	AuCl ₃	3d	trace

^aReactions were conducted with 0.1 mmol of **1a**, 0.1 mmol of pyrrolidine, and 0.12 mmol of TIPS-EBX in 5.0 mL of solvent under an O₂ balloon. ^bYields were determined by GC using biphenyl as the internal standard. ^c40 °C, 10 h.

observed when copper, silver, or iron was used, as result of the ineffective α -vinyldienation by those metals (Table 1, entries 1–3). No ynone was found in the absence of either gold or an amine. Without O₂, the combination of AuCl/AuCl₃ and pyrrolidine led to a decent conversion to a mixture of α -allenyl aldehyde and the α -alkynylated aldehyde.²⁰ The desired ynone product **2a** was obtained in 13% yield (GC) when the reaction was carried out using AuCl₃ in toluene (Table 1, entry 5). AuCl was significantly inferior (Table 1, entry 4). Various secondary amines were examined as well (for a comprehensive conditions survey, see Supporting Information (SI)). Pyrrolidine was the only amine leading to a detectable amount of **2a**. For other amines, the aldol dimerization of the aldehyde was the major side reaction. The solvent screening quickly identified Et₂O as the optimum reaction media. Ligands had a profound impact on the conversion to yrones, with 4,5-diazafluorenone being the most effective. Finally, raising the reaction temperature to 40 °C afforded ynone **2a** in 81% GC yield.

The scope of the aldehydes was studied extensively. For 3-phenylpropanal analogues, substituents of various electronic characteristics on the aromatic ring were well tolerated (Table 2, product **2b**, **2c**, **2e**, **2q**). The reaction was also very effective for various aliphatic aldehydes, especially those bearing useful functional groups, such as ethers, esters, carbamates, imides, olefins, hydroxy, sulfonamide, and heterocycles (Table 2, products **2f**, **2h**, **2i**, **2j**, **2o**, **2p**, **2s–2u**). Generally, the ynone

Table 2. Substrate Scope of the Ynone Synthesis^a

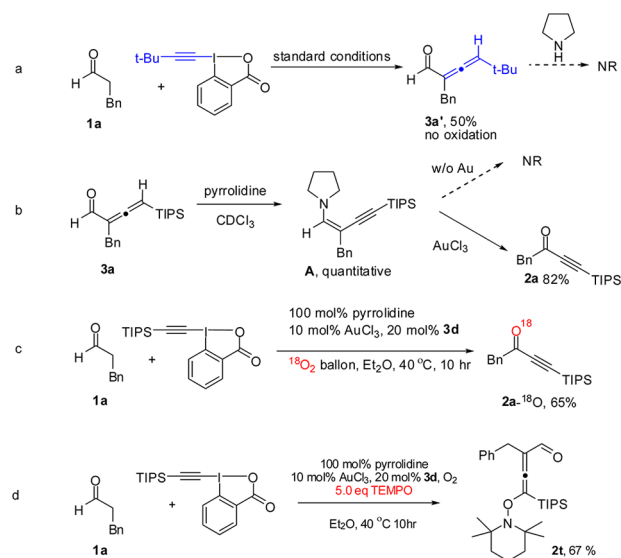


^aIsolated yields.

products **2** were obtained in 60–70% isolated yields. Sterically congested yrones having a secondary carbon chain directly attached to the carbonyl could be accessed using β -branched aldehydes (Table 2, products **2g**, **2k**, **2l**, **2m**, **2n**). No deterioration of yield was observed for these substrates.

Various substituted EBX reagents were also examined. Consistent with our previous report, only silyl substituted EBX reagents were effective for this transformation. When the *t*-Bu-EBX reagent was used, the corresponding *tert*-butyl allenyl aldehyde was isolated in 50% yield (Scheme 2, eq a). This result suggested that the formation of the key ynenamine intermediate was accelerated by the silicon group. Further treating allenyl aldehyde **3a'** with pyrrolidine did not lead to the ynenamine formation even at elevated temperature. In sharp contrast, mixing the allenyl aldehyde **3a** with pyrrolidine in CDCl₃ at rt resulted

Scheme 2. Mechanistic Studies of the C–C Bond Cleavage by Aerobic Oxidation

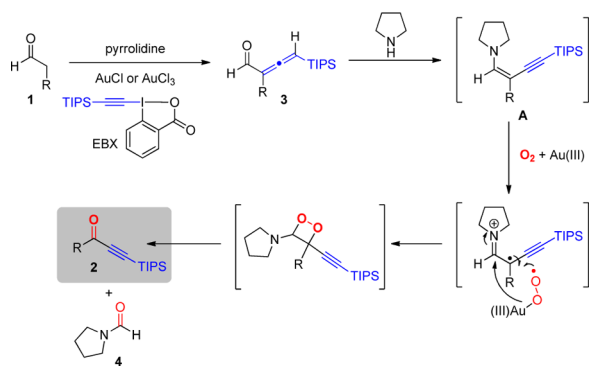


quantitative formation of the ynenamine **A** in 30 min. We reason the facile ynenamine formation of the TIPS substituted allenyl aldehyde is likely due to the stabilization of the enyne moiety by the strong hyperconjugation effect of silicon. The subsequent C–C bond cleavage of **A** did not occur in the absence of gold. Various gold(I) and (III) species catalyzed the ynone formation. A ligand seemed to have a smaller effect in this step compared to the allenyl aldehyde formation.

An $^{18}\text{O}_2$ experiment confirmed that the oxygen of the ynone originated from molecular oxygen and this process is indeed aerobic. When an aldehyde bearing an α -cyclopropane was used as a radical clock, no ynone product was obtained. Instead, multiple decomposition products were observed that bear olefinic protons, indicating the generation of an α -iminium radical. When 5.0 equiv of TEMPO (2,2,6,6-tetramethyl-1-oxypiperidine) was added, the ynone formation was completely inhibited and a coupling product **2t** was isolated in 67% yield, which also supports a free radical pathway for the oxidative C–C bond cleavage.

Based on the aforementioned experimental data, we propose the following mechanism for the ynone formation via C–C bond cleavage by O_2 (Scheme 3).²³ Under the standard conditions, a

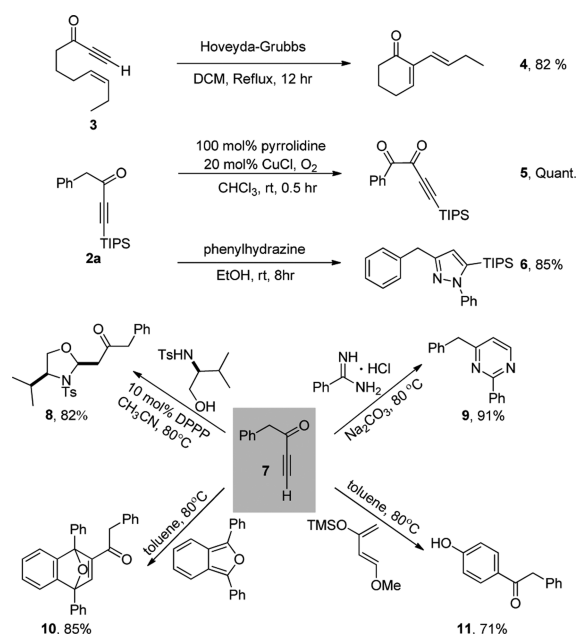
Scheme 3. Proposed Mechanism for the Aerobic C–C Bond Cleavage



smooth α -vinylideneation of aldehyde **1** occurs to give α -allenyl aldehyde **3**, which has been verified experimentally. The allenyl aldehyde continues to react with pyrrolidine to generate the ynenamine intermediate **A**. The subsequent aerobic oxidation of the **A** is believed to occur through the 1,2-dioxetane intermediate,²⁴ which leads to the ynone product **2** via C–C bond cleavage.²⁵ The byproduct pyrrolidine-1-carbaldehyde **4** was detected by HRMS and isolated in good yield. The exact role of gold in the C–C bond cleavage step is not clear. It is likely that gold activates molecular oxygen and facilitates single electron transfer from the electron-rich ynenamine to O_2 .

The TIPS group on the ynone product (such as **2a** and **2f**) can be conveniently removed by treatment with TBAF buffered with acetic acid, furnishing the corresponding terminal alkyne in quantitative yield (see the SI). The synthetic utilities of yrones are demonstrated in Scheme 4. Conjugate diene **4** was synthesized in 82% yield via enyne metathesis from terminal ynone **3**, which was prepared by desilylation of product **2p** from Table 2. The ynone product **2a** was further oxidized to a diketone product **5** quantitatively using a copper catalyst and molecular oxygen.²⁶ The yrones showed synthetic versatility toward various heterocycles. Condensation of **2a** with phenylhydrazine generated trisubstituted pyrazole **6** in 85% yield. The terminal ynone **7** reacted with amino alcohol through a

Scheme 4. Diverse Reactivity of Yrones Readily Available from Aldehydes



bisphosphine catalyzed double-Michael reaction to afford 2,5-disubstituted oxazolidine **8** as a single cis-isomer.²⁷ 2,4-Disubstituted pyrimidine **9** was obtained through an annulation reaction with amidine.^{7b} Ynone **7** also participated in cycloaddition reactions. A Diels–Alder reaction between **7** and 1,3-diphenylisobenzofuran generated polycyclic product **10**.²⁸ Substituted phenol **11** was synthesized by treatment **7** with Danishefsky's diene under thermal conditions.²⁹

In summary, we developed a general synthesis of yrones directly from readily available aldehydes, cheap pyrrolidine, a gold catalyst, and molecular oxygen. The reaction proceeds through an α -vinylideneation reaction by gold/amine synergistic catalysis, followed by *in situ* aerobic cleavage of the C–C bond. The relatively broad substrate scope and the aerobic nature of this method represent a major advance over existing conditions for the synthesis of the highly valuable ynone functionality.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, product characterizations, and copies of all NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

huangyong@pkusz.edu.cn

Notes

The authors declare no competing financial interest.

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