

# A Platinum Open Access Journal for Organic Chemistry

Review

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Arkivoc 2022, part viii, 1-18

# Gold-catalyzed reactions using *N*-propargyl β-enaminones

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#### Dedicated to Morris Maximus on his birthday occasion

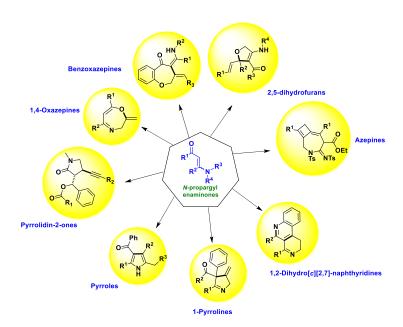
**Received** 05-21-2022

**Accepted** 07-16-2022

Published on line 07-28-2022

#### **Abstract**

Enaminones show unique nucleophilic and electrophilic characteristics exhibited by the amine-alkene-carbonyl system. Gold (I) and Gold (III) complexes are exceptionally potent and superior Lewis acids having a high affinity for  $\pi$  bonds of alkenes, alkynes, and allenes. This review focuses on gold-catalyzed reactions of enaminones and recent advances along with their interesting mechanistic aspects.



**Keywords**: Gold catalysis, 6-endo-dig cyclization, 7-exo-dig cyclization, N-propargyl β-enaminones

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#### 1. Introduction

Transition metal-catalyzed formation of C-C and C-X bonds received considerable attention in modern organic chemistry. Over the past few years, several transition metal catalysts such as Pd, Ni, Ru, Rh have been extensively studied for the construction of these bonds in the literature. Gold-catalyzed organic reactions advanced rapidly and have shown excellent potential to synthesize structurally diverse complex molecules. The recent developments in gold catalysis have heightened because of the unique catalytic properties of gold catalysts and tremendous functional group tolerance. Moreover, gold catalysts are capable to conduct the reactions in a pot manner without isolating intermediates which would allow minimizing the waste of the elements with a high atom economy. Therefore, numerous reactions have been designed based on their reactivity over the last decade. The use of N-propargyl  $\beta$ -enaminones in gold-catalyzed reactions has been rarely mentioned in the literature to date.

As part of our ongoing interest in gold catalysis,  $^{25-28}$  we are interested in reviewing the gold-catalyzed reactions of substituted enaminones. The products achieved throughout this process are versatile building blocks for many heterocyclic molecules. The reactivity associated with the O=C-C=C-NH allows enaminones to exhibit dual electrophilic and nucleophilic characters.  $^{29-33}$  Enaminones are gaining increasing interest because of their unique properties and their importance in organic synthesis as versatile building blocks.  $^{34-48}$  The nucleophilic addition of a variety of functional groups both inter-and intramolecularly toward enaminones utilizing cationic gold (I) and gold (III) complexes have become the most popular in recent years.  $^{49-51}$  This review covers the recent developments in gold-catalyzed reactions using *N*-propargyl  $\beta$ -enaminones to construct interesting molecules.

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#### 2. Benzoxazepines

In 2017, Karunakar group has reported an efficient one-pot synthesis of 3-methylene-3,4-dihydrobenzo[b]oxepinones  $\bf 1$  in the presence of a gold catalyst via intramolecular cyclization of substituted *ortho-O*-propargyl substituted phenyl and naphthyl  $\beta$ -enaminones  $\bf 2$  (Scheme 1). The optimized reactions revealed that the optimum condition for this cyclization reaction was the combination of the catalyst combination of AuClPPh<sub>3</sub>(10 mol %) and AgSbF<sub>6</sub> (15 mol %) as catalytic system using acetonitrile as the solvent, at 28 °C. The reaction proceeded regioselective manner via 7-exo-dig cyclization under gold catalysis under mild conditions giving substituted 3-methylene-3,4-dihydrobenzo[b]oxepinones  $\bf 1$  in good to excellent yields. Under optimized conditions, the reaction tolerates both electron-donating groups and electron-withdrawing groups at substitutions at the R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> positions and gave the products in good yields.

**Scheme 1.** Au-catalyzed synthesis of 3-methylene-3,4-dihydrobenzo[b]oxepinones 1.

It is noted that under the optimized reaction conditions the protocol was successfully applied for the synthesis of substituted benzoxazepine derivatives **4**, **5**, **6**, **7** from alkyne disubstituted enaminones **3** (Scheme 2).

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Scheme 2. Au-catalyzed synthesis of substituted Benzoxazepine derivatives 4-7.

According to mechanistic studies, it proceeds through the coordination of AuCl<sub>3</sub> to the triple bond of **2** following **7**-*exo*-*dig* cyclization to give intermediate **B**, which undergoes protodemetalation to yield substituted benzoxazepine derivatives **1** (Scheme 3).

$$R^{1} \longrightarrow R^{2} \longrightarrow R^{1} \longrightarrow R^{1} \longrightarrow R^{2} \longrightarrow R^{1} \longrightarrow R^{2} \longrightarrow R^{1} \longrightarrow R^{2} \longrightarrow R^{2$$

Scheme 3. Proposed mechanism for the formation of benzoxazepine derivatives 1.

## 3. 1,4-Oxazepines

The same author, in 2015 described the highly efficient synthesis of 1,4-oxazepine derivatives **8** *via* one-pot gold-catalyzed intramolecular cyclization of *N*-propargylic  $\beta$ -enaminones (Scheme 4). The catalytic combination of AuCl<sub>3</sub>(10 mol %) and AgSbF<sub>6</sub> (15 mol %) in methanol was the best optimal condition for this intramolecular cyclization reaction. The substrate scope revealed that *N*-propargylic  $\beta$ -enaminones with electron-donating groups on the benzene rings are well tolerant than the electron-withdrawing groups.

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**Scheme 4**. Au-catalyzed synthesis of 1,4-oxazepine derivatives **8**.

Mechanistically, the triple bond of the *N*-propargylic  $\beta$ -enaminones **9** is activated by Au to form a  $\pi$ -complex intermediate **A**, which then undergoes *7-exo-dig* cyclization *via* nucleophilic attack of carbonyl oxygen to give intermediate **B.** Subsequently, an intramolecular proto-demetalation leads to the product **8** (Scheme 5).

$$R^2$$
 $R^2$ 
 $R^2$ 

Scheme 5. Proposed mechanism for the formation of 1,4-oxazepine derivatives 8.

## 4. Pyrrolidin-2-ones

In 2013, the group of Hashmi published an elegant and novel protocol for the synthesis of 3,4-disubstituted Pyrrolidin-2-ones using Au-catalyzed tandem 1,3-acyloxy migration and 1,5-acyloxy migration of 1-(N-methylcinnamamido)pent-3-yn-2-yl acetates **11** (Scheme 6) which leads a formal 1,6-acyloxy migration.<sup>50</sup> The authors declared that this 1,6-acyloxy migration was the first example of migration reaction. Thus, the optimized reactions revealed that the optimum condition for this cyclization reaction was the combination of [IPrAuCl]/AgSbF<sub>6</sub> as a catalytic system using dichloroethane as the solvent, at 80 °C. The substrate scope appears that the propargylic esters **11** bearing methyl, n-butyl, n-pentyl, cyclopropyl, phenyl group, fluoro, chloro, and pivaloyl functional groups afford substituted pyrrolidin-2-ones **10** in good to higher yields.

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$$R^{1} = CH_{3}, tert$$
-butyl 
$$R^{2} = n$$
-butyl,  $n$ -pentyl, cyclopropyl, cyclohexyl, phenyl 
$$R^{3} = F, Cl$$

$$R^{2} = R^{2}$$

$$R^{2} = R^{2}$$

$$R^{3} = R^{2}$$

Scheme 6. Au-catalyzed synthesis of 3,4-Disubstituted Pyrrolidin-2-ones 10.

Mechanistically, the triple bond activated by the gold (I) complex to form an allene intermediate  $\bf B$  through [3,3]-sigmatropic rearrangement of intermediate  $\bf A$ . Subsequently, gold (I) complex would end up at the  $\pi$  face *anti* to the acetoxy group followed by a direct nucleophilic attack of the alkene to give  $\bf C$ . This stereoselectivity leads to the formation of vinylgold intermediate with a trans arrangement of both substituents on the lactam ring and a trans configuration of the olefin. Finally, the triple bond would be regenerated by elimination of the gold catalyst and the ester group through acyloxy shift from eightmembered ring  $\bf D$  or a sixmembered ring  $\bf E$  (Scheme 7).

Scheme 7. Proposed mechanism for the formation of Pyrrolidin-2-ones 10.

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#### 5. Pyrroles

Saito and Hanzawa et al. disclosed mild and practical access to tri- and tetrasubstituted pyrroles via the amino-Claisen rearrangement of *N*-propargyl  $\beta$ -enaminone derivatives **13** (eq. 4).<sup>54</sup> The careful optimization reactions revealed that the optimum reaction condition for this transformation was the addition of [(IPr)Au(MeCN)]BF<sub>4</sub> (5 mol%) to a solution of *N*-propargyl  $\beta$ -enaminone derivatives **13** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Under the optimized conditions, the reaction tolerates various substituted *N*-propargyl  $\beta$ -enaminone derivatives and gave the corresponding substituted pyrroles **12** after the basic workup in good yields (Scheme 8). However, the formation of **14** was observed in 38 % if Y= Me and R<sup>1</sup> = Ph.

$$\begin{array}{c} \textbf{O} \\ \textbf{Y} \\ \textbf{N} \\ \textbf{Ts} \end{array} \qquad \begin{array}{c} 1. \ [(\text{IPr})\text{Au}(\text{MeCN})] \text{BF}_4 \ (5 \ \text{mol}\%) \\ \hline \text{CH}_2\text{Cl}_2, \ \text{rt} \\ 2. \ \text{KOH/ MeOH-THF} \end{array} \qquad \begin{array}{c} \textbf{R}^1 \\ \textbf{N} \\ \textbf{H} \end{array} \qquad \begin{array}{c} \textbf{N} \\ \textbf{Ts} \end{array}$$

Scheme 8. Au-catalyzed synthesis of pyrroles 12.

In other hand the reaction of enaminoester **15** under the Au-catalyzed optimized conditions leads to the formation of dihydropyridine **17** in 86% yield. Interestingly, the improvement in the yield of **16** was observed if increasing the ratio of HFIP as a cosolvent (Scheme 9).

**Scheme 9.** Au-catalyzed synthesis of pyrroles **16.** 

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## 6. 3-Methylene-1-pyrrolines

In 2014, Karunakar group reported the formation of a wide variety of 3-methylene-1-pyrrolines with quaternary stereocenters and exocyclic double bonds from the reaction of N-propargylic  $\beta$ -enaminones and arynes under gold(I) catalysis (Scheme 10). The optimization study revealed that the optimum reaction for this transformation was addition of AuCIPEt<sub>3</sub> (10 mol%), CsF (3 equiv) and AgSbF<sub>6</sub> (15 mol%) in CH<sub>3</sub>CN at 80 °C. Under the optimized conditions, the reaction tolerates various substituted N-propargyl  $\beta$ -enaminone derivatives and gave the corresponding 3-methylene-1-pyrrolines derivatives **18** in moderate to good yields.

$$\begin{array}{c} \textbf{R}^{1} & \textbf{N} & \textbf{TMS} & \begin{array}{c} \textbf{AuCPEt}_{3}/AgSbF6 \\ (10 \text{ mol}\%/15 \text{ mol}\%) \\ \textbf{CSF} \ (3 \text{ equiv}) \\ \textbf{CH}_{3}\textbf{CN}, \ 80 \ ^{\circ}\textbf{C} \end{array}$$

**Scheme 10**. Au-catalyzed synthesis of 3-Methylene-1-pyrrolines **18**.

In other hand, the scope of the naphthyne substrate **21** with *N*-propargylic  $\beta$ -enaminones **19** for the synthesis of pyrroline derivatives **22** was also conducted (Scheme 11). Under the same optimization conditions, the reaction afforded the desired products in good yields. When the reaction was conducted with *N*-propargylic  $\beta$ -enaminones **19** and methyl substituted benzyne **23** the inseparable mixture of *m*-Me and *p*-Me isomers **24** and **25** (1:1) were observed in 64-68% yields (Scheme 12).

O R<sup>1</sup> + TMS 
$$\frac{\text{AuCPEt}_3/\text{AgSbF6}}{(10 \text{ mol}\%/15 \text{ mol}\%)}$$
  $\frac{\text{CsF (3 equiv)}}{\text{CH}_3\text{CN, 80 °C}}$   $\frac{\text{R}^1}{\text{R}^2}$   $\frac{\text{R}^2}{\text{N}}$   $\frac{\text{R}$ 

**Scheme 11.** Au-catalyzed synthesis 3-Methylene-1-pyrrolines **22**.

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**Scheme 12.** Au-catalyzed synthesis 3-Methylene-1-pyrrolines **24** and **25**.

According to mechanistic studies, the reaction between substrate **19** and benzyne in the presence of the gold catalyst AuCl<sub>3</sub>/AgSbF<sub>6</sub> (10/15 mol%) to form an intermediate **A**, which then undergoes *5-exo-dig* cyclization to give intermediate **B**. Subsequently, an intramolecular proto-demetalation leads to the product **18**.

Scheme 12. Proposed mechanism for the formation of 3-Methylene-1-pyrrolines 18.

# 7. 1,2- Dihydro[c][2,7]naphthyridines

Recently gold-catalyzed intramolecular cyclization/condensation of 2-aminophenyl prop-2-yn-1-yl enaminones was reported by Karunakr and co-workers (Scheme 13).<sup>56</sup> In this study, 1,2-dihydro[c][2,7]naphthyridines **29** were obtained in good yields by reaction of 2-aminophenyl prop-2-yn-1-yl enaminones *via 6-endo*-dig cyclization and condensation in the presence of AuClPPh<sub>3</sub> (5 mol%)/AgSbF<sub>6</sub> (5 mol%) and acetic acid (5 mol%) in acetonitrile as a solvent at room temperature. Under optimized conditions, the reaction tolerates substitutions such as electron-withdrawing, electron-donating, aliphatic, alicyclic, and heteroaryl on 2-aminophenyl prop-2-yn-1-yl enaminone **27** and gave the products **28** under exceptionally mild conditions.

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$$R^{1} = C_{6}H_{5}, 4-Me-C_{6}H_{4}, C_{5}H_{11}, cyclohexyl, 2-napthyl \\ R^{2} = C_{6}H_{5}, 4-Br-C_{6}H_{4}, 2,4-dichloro-C_{6}H_{3}, 4-CN-C_{6}H_{4}, 4-F-C_{6}H_{4}, 4-CF_{3}-C_{6}H_{4} \\ 4-MeO-C_{6}H_{4}, 4^{-t}Bu-C_{6}H_{4}, 4-Et-C_{6}H_{4}, 4-Br-C_{6}H_{4} \\ 4-Br-C_{6}H_{4}, 4-Br-C_{6}H_{4}, 4-Br-C_{6}H_{4} \\ 4-Br-C_{6}H_{4}, 4-Br-C_{6}H_{4}, 4-Br-C_{6}H_{4} \\ 4-Br-C_{6}H_{4}, 4-Br-C_{6}H_{4}, 4-Br-C_{6}H_{4} \\ 4-Br-C_{6}H_{4}, 4-Br-C_{6}H_{4}, 4-Br-C_{6}H_{4} \\ 4-Br-C_{6$$

**Scheme 13.** Au-catalyzed synthesis of 1,2- Dihydro[c][2,7]naphthyridines **28.** 

The authors proposed the mechanism by coordinating gold catalyst with the triple bond of 2-aminophenyl prop-2-yn-1-yl enaminone **29** gave the intermediate **A** followed by nucleophilic attack of the  $\alpha$ -carbon center of carbonyl through *6-endo-dig* cyclization producing the intermediate **B** (Scheme 14). In the presence of an acid, intermediate **B** would undergo condensation and protodeauration to produce intermediate **C**. Finally through aromatization and double bond isomerization gave 1,2-dihydrobenzonaphthyridine derivatives.

**Scheme 14.** Proposed mechanism for the formation of 1,2- Dihydro[c][2,7]naphthyridines **28.** 

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### 8. Azepines

More recently, Sahoo's research group reported a new protocol for synthesis of unknown cyclobutene-fused azepine heterocycles **30** by cycloisomerization of corresponding stable alkyne tethered ketene *N*, *N*-acetals **31** in the presence of [JohnphosAu(I) (MeCN)] $^+$ SbF $_6^-$  as a catalyst **32** (Scheme 15). Thus, the careful analysis of the optimized reactions revealed that the optimum condition for this transformation was the addition of [JohnphosAu(I) (MeCN)] $^+$ SbF $_6^-$  (3.0 mol%) in dichloromethane solvent at room temperature. The reaction tolerated various functional groups and produced the desired products in moderate to good yields.

TsN 
$$R$$
 Catalyst 32 (3 mol%)

DCE, rt, 4 h

Ts NTs

R

31

R = Aryl, heteroaryl

Scheme 15. Au-catalyzed synthesis of cyclobutene fused azepines 30.

In this study, the authors also evaluated the mechanistic study for this transformation. To determine the intermediates of the reaction, the authors monitored the reaction by <sup>1</sup>H NMR spectroscopy. Among the data that could be obtained by <sup>1</sup>H NMR spectroscopy, the most relevant for the proposal was shown in Scheme 16.

**Scheme 16.** Proposed mechanism for the formation of Azepines **30.** 

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### 9. 2,5-Dihydrofurans

In 2013, the Karunkar group reported a new protocol for the synthesis of 2,5-dihydrofuran derivatives **33** using Au-catalyzed intramolecular rearrangement and cyclization of *O*-propargyl  $\beta$ -enaminones **34** (Scheme 17). The careful analysis of the optimized reaction conditions revealed that the optimum reaction condition for this reaction was the addition of AuClPEt<sub>3</sub> (10 mol%) / AgSbF<sub>6</sub> (15 mol%), at 28 °C, to a solution of *O*-propargyl  $\beta$ -enaminones in CH<sub>3</sub>CN. The scope of the reaction appears that *O*-propargyl  $\beta$ -enaminones **34** bearing electron-donating and electron-withdrawing groups tolerate the reaction and produced the 2,5-dihydrofuran derivatives **33** in good to excellent yields.

 $R^1$  = Ph, 4-MeC<sub>6</sub>H<sub>4</sub>, 1.2.3-trimethoxybenzene, 1,2-dichlorobenzene 29 examples (70-92%)

 $R^2$  = Ph, n-pentane

 $R^3$  = Ph, cyclohexyl, thiophene, 4-Me-C<sub>6</sub>H<sub>4</sub>, 4-OMe-C<sub>6</sub>H<sub>4</sub>

 $R^4$  = Ph, *n*-methyl, *n*-benzyl, tryptamine, cyclopentyl

**Scheme 17.** Au-catalyzed synthesis of 2,5-Dihydrofurans **33**.

According to mechanistic studies (Scheme 18), it proceeds through the coordination of gold catalyst coordinates with substrate **35**, following the nucleophilic attack of carbonyl oxygen onto the activated triple bond to give intermediate D, which undergoes cyclization and rearrangement to yield 2,5-dihydrofuran derivatives **34**.

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**Scheme 18.** Proposed mechanism for the formation of 2,5-Dihydrofurans **33**.

#### 10. Conclusions

In summary, we have discussed the gold-catalyzed recent advance reactions using enaminones for the construction of nitrogen-based heterocycles. As illustrated, high atom economy and shorter synthetic routes are the key features of these reactions. The present methodologies are meaningful and particularly attractive for the fact that those *N*-heterocycles are the structural component of a vast number of biologically active natural and unnatural compounds. Also interesting is the fact that most of the cyclization reactions covered in this review could be easily adapted to the gram-scale synthesis of *N*-heterocycles. We believe that these salient features of enaminones in the synthesis of *N*-heterocycles will further elicit widespread attention in the quest for more applications and utilities, serving as a powerful and versatile substrate in the synthesis of important *N*-heterocycles and complex natural products.

# **Acknowledgements**

S.G. thanks to UGC for his senior research fellowship and AcSIR. V.G. thanks to Purdue University for his postdoctoral fellowship. K.S thanks to HOD Prof. A. K. Prasad, University of Delhi for his support and thanks to Dr. Ramendra Pratap, University of Delhi for his valuable suggestions.

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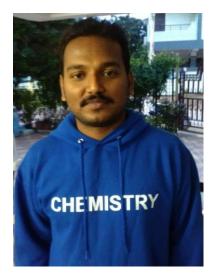
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