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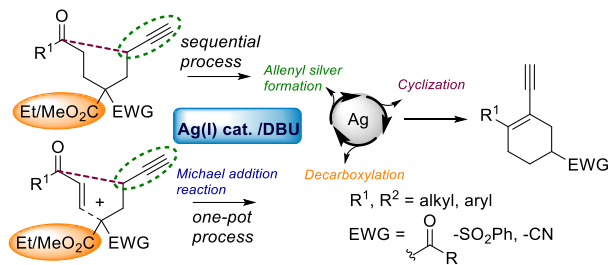
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Access to conjugated enynes via allenyl silver formation/cyclization/decarboxylation reaction catalyzed by silver carbonate(I)

Bao Yu^a, Mohamed Selkti^a, Janick Ardisson^a, Marie-Isabelle Lannou^{a*}, Geoffroy Sorin^{a*}

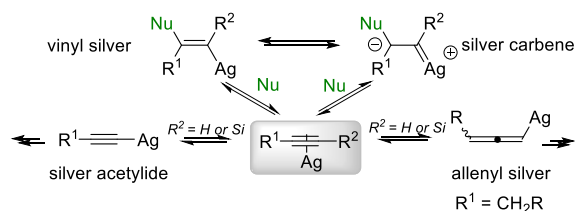
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ABSTRACT: Herein, we develop a novel and straightforward access to cyclic conjugated enynes catalyzed by silver carbonate/DBU from readily available substrates with good yields. The reaction is easy to set-up, broad in scope and can also be conducted in a one-pot fashion from easily accessible substrates through a sequence Michael addition reaction/cyclization. Based on our previous works, the mechanism proposed would involve an allenyl silver intermediate and decarboxylation reaction.

Since the last two decades, homogeneous silver salts catalysis has renewed a great interest in synthetic chemistry highlighted by a broad variety of reactions reported in the literature.¹ Silver salts possess versatile activities and were, for example, commonly used either for their ability to activate heteroatoms thanks to their Lewis acidity,² their oxidizing properties or for their halogenophilicity in metal catalyzed C-C bond formation.^{3,4} In addition, due to its electronic configuration [Kr] 4d¹⁰5s¹ in group 11, silver belongs to “coinage metals” and therefore, possess similar activity as gold towards the π -activation of carbon-carbon multiple bonds. However, even if silver is cheaper than gold, it is almost as scarce and therefore, performing catalytic reactions with such metals is a crucial point regarding the depletion of the natural resources on earth.⁵ Among the different types of activation by silver salts, we can underline those targeting alkynes, which have been reviewed or published in the literature these last years.⁶ Remarkably, silver π -acidity allowed very interesting and promising transformations from alkynes through different C-C triple bond activation (Scheme 1).

Scheme 1. Different pathways possible from alkyne complexed by silver salts

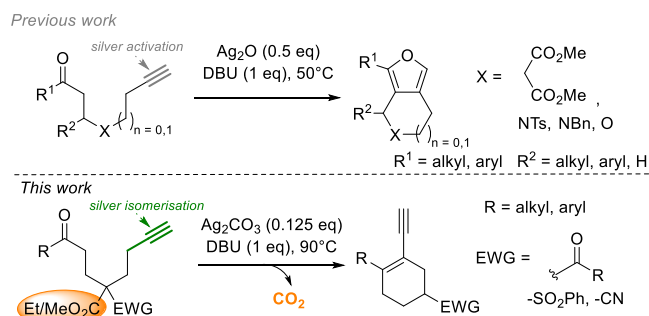


Hence, from alkynes, the formation of silver acetylides,⁷ vinyl silver or silver carbenes can be envisioned.^{8,9} In addition, we

recently highlighted the propensity of silver oxide(I) to isomerize terminal or silylated alkynes into allenyls silver in the synthesis of 2,3-dihydrofurans derivatives.¹⁰ Previous works reported by Zhang *et al.* also mentioned this type of isomerization catalyzed by silver salts from propargylamides.¹¹ Nevertheless, the formation of allenyl silver intermediates are really scarce and therefore very little attention was paid towards their reactivities. To the best of our knowledge, they have mainly been explored by the Vermeer group through the intermolecular addition of allenyl silver species onto few electrophiles.¹² However, no intramolecular reaction involving allenyl silver species has been reported prior to our work on dihydrofuran derivatives (Scheme 1).¹⁰

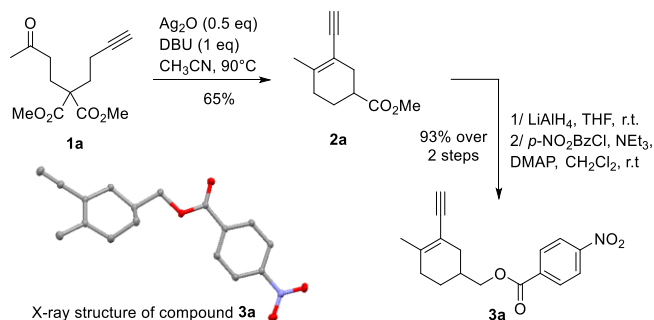
In the course of our previous works on polysubstituted furan synthesis,¹³ we screened substrates with different chain length bearing an alkyne moiety in order to reach 5- or 6-membered rings (Scheme 2). Astonishingly, depending on the substitution pattern of the ketone, different behaviors were observed concerning the cyclization. Indeed, with aromatic ketones, the expected bicyclic furan was obtained as the major product whereas aliphatic ketones mainly led to conjugated enynes. The formation of such cyclic cores appeared particularly interesting since only one step was required to reach complex enyne structures from a readily available malonate using smooth conditions. Moreover, the formation of an allenyl silver intermediate was clearly considered as key point of this unprecedented transformation. Intrigued by this promising result, we decided to pursue further our investigations in order to explore the scope and mechanism of this new transformation.

Scheme 2. Preliminary works



In a preliminary survey, behaviour of the malonate type compound **1a** was studied in acetonitrile in the presence of a combination of $\text{Ag}_2\text{O}/\text{DBU}$. After increasing the temperature to 90°C , we were pleased to find a complete conversion of **1a** into the conjugated enyne **2a** over 12 h. The structure was confirmed by a single-crystal X-ray diffraction analysis of *p*-nitrobenzoyl derivative **3a**,¹⁴ obtained after reduction of ester and subsequent esterification of the resulting alcohol with *p*-nitrobenzoyl chloride (93% yield over two steps, Scheme 3).

Scheme 3. Structure determination



Then, we started the optimization of the reaction conditions, again by choosing compound **1a** as the model substrate (Table 1).

Table 1. Reaction optimization. Full data optimization is available in the ESI.

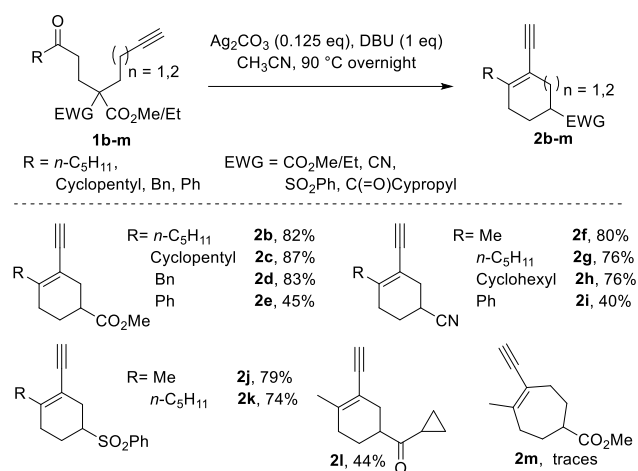
Entry	Silver (eq).	Base	Solvent	Yield*
1	Ag_2CO_3 (0.5)	DBU	CH_3CN	87%
2	Ag_2O (0.5)	DBU	CH_3CN	67%
3	Ag_3PO_4 (0.33)	DBU	CH_3CN	60%
4	AgOTf (1)	DBU	CH_3CN	8%
5	AgNTf_2 (1)	DBU	CH_3CN	23%
6	Ag_2CO_3 (0.5)	K_2CO_3	CH_3CN	36%
7	Ag_2CO_3 (0.5)	Pyrrolidine	CH_3CN	14%
8	Ag_2CO_3 (0.5)	NET_3	CH_3CN	31%
9	Ag_2CO_3 (0.5)	<i>i</i> -Pr ₂ NEt	CH_3CN	30%
10	Ag_2CO_3 (0.5)	DBU	THF	85%
11	Ag_2CO_3 (0.5)	DBU	DMF	67%

12	Ag_2CO_3 (0.5)	DBU	Toluene	68%
13	Ag_2CO_3 (0.5)	DBU	MeOH	44%
14	--	DBU	CH_3CN	0%
15	Ag_2CO_3 (0.5)	--	CH_3CN	9%
16	Ag_2CO_3 (0.25)	DBU	CH_3CN	86%
17	Ag_2CO_3 (0.125)	DBU	CH_3CN	86%
18	Ag_2CO_3 (0.0625)	DBU	CH_3CN	47%

*¹H-NMR yield was calculated by using 1,3,5-trimethoxybenzene as internal standard.

A rapid survey of silver catalysts demonstrated that silver carbonate(I) was the best candidate for this transformation (87% yield, Entry 1). Silver oxide(I) provided the compound **2a** in 67% yield (Entry 2) whereas silver phosphate led to 60% yield (Entry 3). With other silver salts, conversions into product **2a** ranged from insignificant to low with respectively AgOTf (8%, Entry 4) and AgNTf_2 (23%, Entry 5). The role of the base appeared crucial since K_2CO_3 (Entry 6), pyrrolidine (Entry 7), NET_3 (Entry 8) and *i*-Pr₂NEt (Entry 9) afforded poor conversions (respectively 36%, 14%, 31% and 30%). On the contrary, various solvents were well tolerated including THF (85%, Entry 10), DMF (67%, Entry 11) and toluene (68%, Entry 12). However, we noticed a slight decrease of the yield by using protic solvent like MeOH (44%, Entry 13). Finally, control reactions highlighted the mandatory combination of both reagents since no reaction occurred without silver carbonate, (0%, Entry 14) and a dramatic drop of yield was observed when the reaction was conducted without DBU (9%, Entry 15). To our delight, similar good yields were obtained by reducing the loading of Ag_2CO_3 to 0.25 equivalent (Entry 16, 86%) or to 0.125 equivalent (Entry 17, 86%). However, a collapse of yield was observed when 0.0625 equivalent of silver carbonate(I) was employed (Entry 18, 47%). At this stage, we tried to add oxidative agent in order to restore the catalytic species. Unfortunately, whatever the oxidant tested (O_2 , $\text{PhI}(\text{OAc})_2$, CeO_2 or $\text{K}_2\text{S}_2\text{O}_8$), we never succeed in improving the yield.¹⁵ As a conclusion, the best combination for this reaction turned out to be: Ag_2CO_3 (0.125 eq), DBU (1 eq), CH_3CN , under reflux over 12h.

Scheme 4. Scope of the reaction



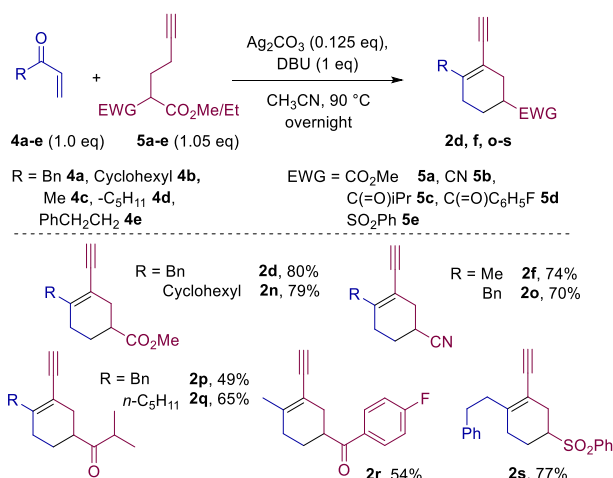
With the optimized reaction conditions in hand, we subsequently explored the substrate scope of our method by modifying the substitution pattern on the ketone as well as on the malonate-type part (Scheme 4). For substrates bearing a β -diester

moiety, *n*-pentyl (**1b**) or cyclopentyl (**1c**) or benzyl (**1d**) derivatives afforded the corresponding enynes (**2b**, **2c** and **2d**) with satisfactory yields (82 to 87%), whereas aromatic ketones (R = Ph, **1e**) resulted in moderate yield (**2e**, 45%). This drop of yield is explained by the competitive formation of the bicyclic furan (29%, isolated yield). This result is consistent with our preliminary work (scheme 2).¹³ Hence, the main difference between aryl and alkyl ketones arises from the pKa values of the hydrogen in α position to the ketone. Competitive formation of the furan is more prone to occur as the pKa value of the α -hydrogen diminishes; the balance between the two competitive reactions being sometimes very tight.

A similar behavior was also observed with β -cyanoesters, since various alkyl ketones, comporting either methyl (**1f**), *n*-pentyl (**1g**) or cyclohexyl (**1h**) group successfully furnished the desired products (**2f**, **2g** and **2h**) (Scheme 4) in good yields (80%, 76% and 76%, respectively), while cyclization of the precursor bearing a phenyl group (**1i**) only resulted in moderate yield (**2i**, 40%). To our delight, this transformation also delivered β -phenylsulfonylesters derivatives (**2j** and **2k**) with good yields (79% and 74%, respectively from precursors **1j** and **1k**). Interestingly, these reaction conditions were also found to be suitable for more hindered cyclopropyl ketone (**1l**) even if the expected product **2l** was only obtained in moderate yield (44%). Regarding the low difference of the pKa of the hydrogen in α position to the ketone in **1l** and **2l**, only steric factor at that position could help to discriminate **1l** and **2l**, which explains the lower yields obtained while carrying the cyclization on **1l**. Finally, the case of longer chain systems was investigated: while submitting malonate **1m** having a 6-C instead of 5-C spacer between the ketone and the alkyne moiety, only traces of the expected product **2m** were detected by ¹H NMR even by increasing the loading of Ag₂CO₃ to 2 equivalents or heating in a sealed tube at 110 °C.

In order to set up a flexible, straightforward and more environmentally friendly process, we focused on a one-pot procedure Michael addition/cyclization. To this aim, we decided to take advantage of the use of DBU, which was previously identified by Kim and co-workers as an efficient base for promoting Michael addition reactions.¹⁶ In our case, DBU could sequentially promote the 1,4-addition onto α,β -unsaturated ketone before being engaged in the cyclization process. To this aim, we applied our optimized conditions onto various Michael acceptors in the presence of malonates **5a-e** (Scheme 5).

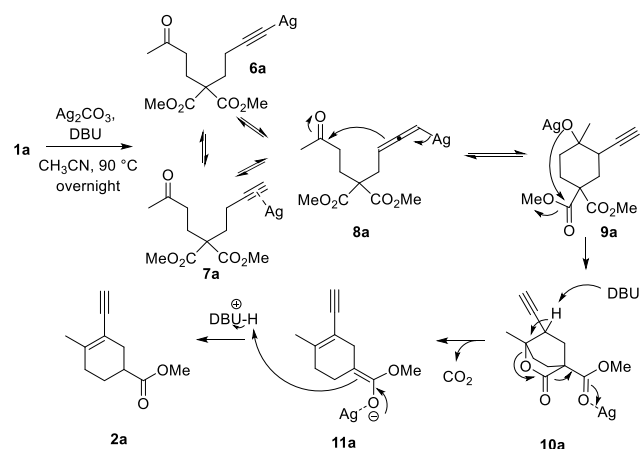
Scheme 5. One-pot process



To our delight, the cyclization conditions were found suitable for a one-pot process. First trial involving malonate **5a** and 1-phenylbut-3-en-2-one **4a** afforded **2d** with a similar yield (80%) as in the two-step process (83%); malonate **5a** also reacted smoothly with 1-cyclohexylprop-2-en-1-one **4b** to afford **2n** in good yield (79%). Likewise, alkyne bearing a β -cyanoester moiety **5b** was able to react with methylvinyl ketone **4c** and 1-phenylbut-3-en-2-one **4a** to afford expected compounds in good yields (**2f**: 74% vs. 80% for the two-steps process and **2o**: 70%). Interestingly, one-pot process was also found to be appropriate in the case of β -ketoester **5c** comporting an hindered isopropyl ketone; hence while reacting with **4a** and **4d**, **2p** and **2q** were provided with satisfying yields (respectively 49 % and 65 %). In the same manner, the reaction proceeded with β -ketoester **5d** comporting a benzylic ketone to afford **2r** in 54% yield, this moderate yield can be explained by difficulties encountered during the purification step. Finally, the reaction was successfully carried out with β -phenylsulfonylester **5e** delivering **2s** in 77% yield. As a conclusion, this one-pot process Michael addition/cyclization revealed especially efficient since on two selected examples, yields proved to be similar to those obtained in the two-step process. Moreover, this transformation evidenced a good functional group tolerance whether on the Michael acceptor (**4a-e**) or on the alkyne bearing a malonate-type moiety (**5a-e**).

On the basis of our previous work on 2,3-dihydrofuran and furans^{10,13} a plausible reaction mechanism for the cyclic enyne core synthesis is suggested in Scheme 6.¹⁷

Scheme 6. Proposed mechanism

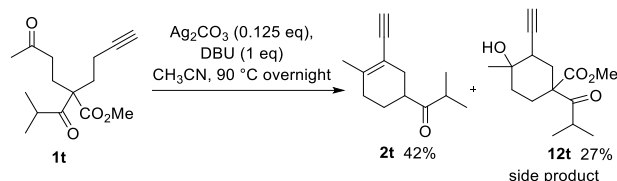


The first step would be the formation of the alkynyl silver **6a** from alkyne **1a**. Thanks to the support of DFT calculation performed in the course of the synthesis of dihydrofurans,¹⁰ we could assume that species **6a** is in equilibrium with the allenyl silver **8a** through the transitory formation of the silver alkyne complex **7a**. Due to the very weak nucleophilicity of intermediate **6a**, alkynyl silver could neither react in intra- nor in intermolecular fashion. In contrast, the allenyl silver **8a** would preferentially attack the ketone leading to the silver alkoxide **9a**. A retro-addition can reasonably be envisioned rendering this cyclization step reversible too. The hydroxylate thus generated **9a** would attack one of the ester to form the highly strained lactone **10a**. Release of CO₂ from the tricyclic adduct **10a** would be achieved by deprotonation in α -position of the alkyne and subsequent fragmentation/decarboxylation reaction. This irreversible transformation would push the equilibrium towards the formation of the six-membered ring **11a**. This fragmentation step

would constitute the driving force of the reaction. The newly formed silver enolate could be reprotonated by the conjugated acid of the DBU yielding the final compound **2a**.

Interestingly, during our scope investigation, we isolated compound **12t** in 27% from isopropyl ketone **1t** (Scheme 7).

Scheme 7. Proof of mechanism



At this stage, we presumed that tertiary silver alkoxide was partially *syn*periplanar to the ester, yielding **2t** and partially *anti*-periplanar. In this latter case, it was unable to react with the ester moiety, preventing the second cyclization and thus interrupting the mechanism pathway to provide **12t**. This observation reinforced the mechanism proposed in Scheme 6.

In summary, we have developed a new method for the synthesis of conjugated enynes by a silver carbonate-catalyzed cyclization reaction, conducted for the first time in the presence of DBU. The conditions developed herein are mild, open-air, easy to set-up and tolerate a wide variety of substituted malonate-type systems (nitrile, aliphatic or aromatic ketone, phenylsulfone). Interestingly, we succeeded to extend the conditions to a tandem one-pot process, which is more environmentally friendly and requires even less elaborated substrates, some of them being commercially available. Noteworthy, we assumed that the reaction could proceed with other functional groups such as polar functional groups, substituted alkyls or benzyls, (hetero)aryls since the only crucial point is the pKa value of the H in α position to the ketone. However, functional groups lowering this value would promote the unwanted formation of furan derivatives.

Based on our previous works and results, a plausible mechanism involving an allenyl silver intermediate and a decarboxylation reaction was proposed. However, switching the reactivity towards ene-yne cycloadducts from aromatic ketones appeared more challenging since the competitive formation of furane derivatives spontaneously occurs as described in our previous work. Investigation of new conditions are currently underway in our laboratory to fix this issue.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General information, reaction optimization, catalytic attempts, preparation of the cyclization precursors, cyclization reactions, details on mechanism, ^1H , ^{13}C and ^{19}F NMR spectra (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. /

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(17) For more details on the proposed mechanism, see supporting information.
