Cycloaddition reactions

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Synthesis of Azepine Derivatives by Silver-Catalyzed [5+2] Cycloaddition of γ-Amino Ketones with Alkynes**

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The cycloaddition reaction is a fundamental and powerful transformation for the construction of numerous complex ring systems in organic synthesis.[1–5] This process is most frequently used to prepare five- and six-membered ring systems.[1] However, approaches using a cycloaddition strategy for constructing seven-membered ring systems, particularly seven-membered heterocyclic ring systems, are much less abundant.[1–5] The difficulties of such an approach are likely caused by a combination of entropic factors and the presence of non-bonding interactions in the transition state. Despite the impressive challenges in this field, the continuing identification of bioactive natural products that contain a seven-membered ring has led to considerable efforts to establish valuable cycloaddition methods for their construction.[1–5] Particular focus has been put on the synthesis of azepine derivatives,[4,5] because these are important skeletal units that are found in numerous natural products and in compounds with important chemical, biological, and medicinal properties (Figure 1).[6]

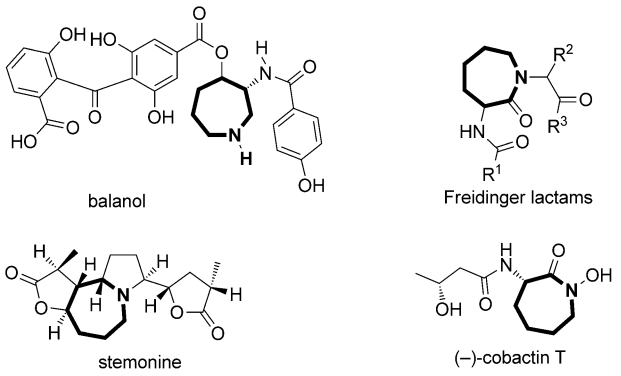
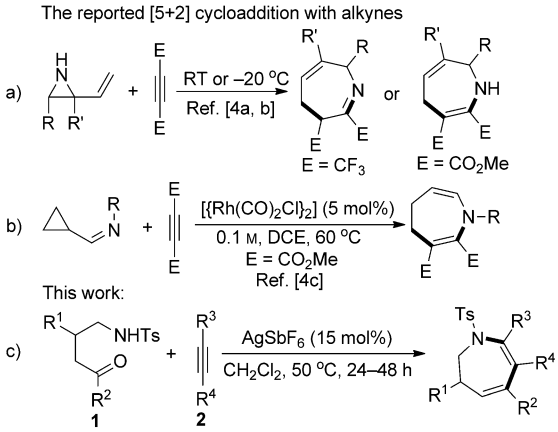


Figure 1. Examples of important azepines.

Among the reported cycloaddition[1–5] and classical approaches[7] toward azepine derivatives, [5+2] cycloaddition reactions with alkynes are particularly straightforward and highly selective; however, these transformations are quite rare and are restricted to electron-poor alkynes.[4] In 1967, Stogryn and Brois described a new [5+2] cycloaddition reaction of 2,3-divinylaziridine with hexafluoro-2-butyne to synthesize the corresponding azepine at room temperature [Scheme 1 a].[4a] Subsequently, Hassner and co-workers



Scheme 1. The [5+2] cycloaddition reaction with alkynes. Ts = Tosyl.

extended the scope of the [5+2] cycloaddition reaction to another electron-deficient alkyne, dimethyl acetylenedicarboxylate, which was converted even at −20 °C.[4b] In 2002, Wender and co-workers first reported an efficient transition-metal-catalyzed hetero-[5+2] cycloaddition of cyclopropyl imines with dimethyl acetylenedicarboxylate, leading to dihydroazepine compounds [Scheme 1 b].[4c] Thus, the development of a general and convenient [5+2] cycloaddition using common alkynes to azepine derivatives remains highly desirable. Herein, we report a new silver-catalyzed tandem [5+2] cycloaddition method using simple and readily available alkynes with γ-amino ketones,[8] which results in the corresponding azepine derivatives in moderate to good yields [Scheme 1 c].[9]

Our investigations began by choosing 4-methyl-*N*-(4-oxo-2,4-diphenylbutyl)benzenesulfonamide (**1a**) and phenylacetylene (**2a**) as the reaction partners for the optimization of the reaction conditions (Table 1). Initially, substrate **1a** was treated with alkyne **2a** and $AgSbF_6$ (15 mol%) in CH_2Cl_2 at room temperature for 72 h, providing the desired 2,3-dihydro-1*H*-azepine **3** in 54% yield (entry 1). Screening revealed that the reaction benefits from an elevated reaction temperature:

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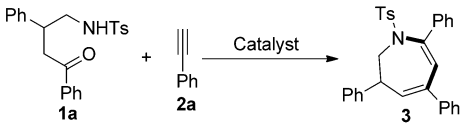
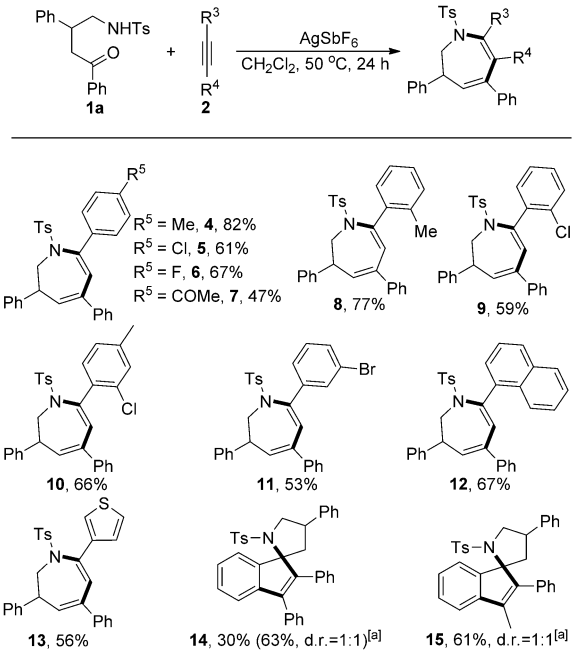
Table 1: Optimization of the reaction conditions.[a]



Entry	Catalyst (mol%)	Solvent	T[b] [°C]	t [h]	Yield[c] [%]
1	$AgSbF_6$ (15)	CH_2Cl_2	RT	72	54
2	$AgSbF_6$ (15)	CH_2Cl_2	30	48	67
3	$AgSbF_6$ (15)	CH_2Cl_2	50	24	86
4	$AgSbF_6$ (15)	CH_2Cl_2	60	24	86
5	$AgSbF_6$ (20)	CH_2Cl_2	50	24	85
6	$AgSbF_6$ (10)	CH_2Cl_2	50	24	56
7	–	CH_2Cl_2	50	24	0
8	$AgBF_4$ (15)	CH_2Cl_2	50	24	trace
9	$AgNO_3$ (15)	CH_2Cl_2	50	24	trace
10	AgOTf (15)	CH_2Cl_2	50	24	10
11	$Cu(OTf)_2$ (15)	CH_2Cl_2	50	24	trace
12	$AgSbF_6$ (15)	CH_2ClCH_2Cl	50	24	79
13	$AgSbF_6$ (15)	toluene	50	24	13
14	$AgSbF_6$ (15)	MeCN	50	24	9
15[d]	$AgSbF_6$ (15)	CH_2Cl_2	50	72	83
16	HBF_4 (15)	CH_2Cl_2	50	24	8
17	HOTf (15)	CH_2Cl_2	50	24	10
18	HOAc (15)	CH_2Cl_2	50	24	trace
19[e]	$AgSbF_6$ (15)	CH_2Cl_2	50	24	trace

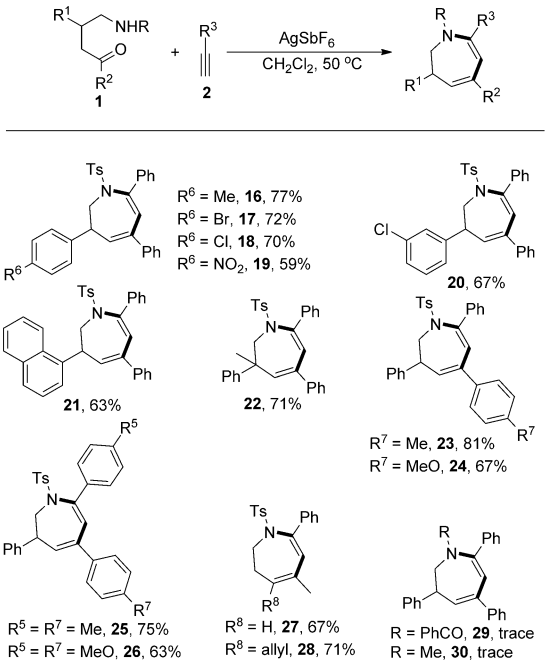
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), and solvent (2 mL) under argon atmosphere for 24 h. Some by-products, including amine-decomposition products and an alkyne-hydration product (acetophenone), were observed by GC-MS analysis. [b] The temperature of the oil bath. [c] Yields of isolated products. [d] **1a** (10 mmol, 3.935 g) and **2a** (18 mmol). [e] One equivalent of NaOAc, Na_2CO_3, or Et_3N was added as a base.

The yield of azepine **3** was increased to 67% after 48 h when the reaction was carried out at 30°C (entry 2), and to 86% after 24 h at either 50°C or 60°C (entries 3 and 4). These results encouraged us to evaluate the amount of $AgSbF_6$ employed (entries 4–6); we found that a $AgSbF_6$ loading of 15 mol% gave the best result. Notably, the reaction does not take place in the absence of a metal catalyst (entry 7). Subsequently, a number of other catalysts, including $AgBF_4$, $AgNO_3$, AgOTf, and $Cu(OTf)_2$, were tested (entries 8–11). However, they displayed rather poor catalytic activity in the reaction. In contrast to these catalysts, $AgSbF_6$ is generated from $HSbF_6$, a superacid; thus $AgSbF_6$ has some special properties: It is a stronger Lewis acid than the other Ag salts, such as $AgBF_4$, $AgNO_3$, and AgOTf, and the silver ions are attached to the SbF_6^- ion by fluoride bridges to form a distorted octahedron, which avoids close Ag^+/Ag^+ contacts.[10] Among the solvents examined, CH_2ClCH_2Cl was found to be an excellent medium for the reaction (entry 12), as the use of other solvents, including toluene and MeCN, led to diminished yields (entries 13 and 14). A good yield can achieved even when using a 10 mmol scale (**1a**), by prolonging the reaction time (entry 15). Three Brønsted acids, HBF_4, TfOH, and HOAc, were used to replace $AgSbF_6$: Both HBF_4 and TfOH have low catalytic activity for the reaction, and HOAc does not catalyze this transformation (entries 16–18). The presence of a base completely suppressed the reaction (entry 19).



Scheme 2. Scope of alkynes **2**. Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $AgSbF_6$ (15 mol%), and CH_2Cl_2 (2 mL) at 50°C under argon atmosphere for 24 h. [a] Both $[\{RhCpCl_2\}_2]$ (5 mol%) and $Cu(OAc)_2$ (50 mol%) were added at 70°C.

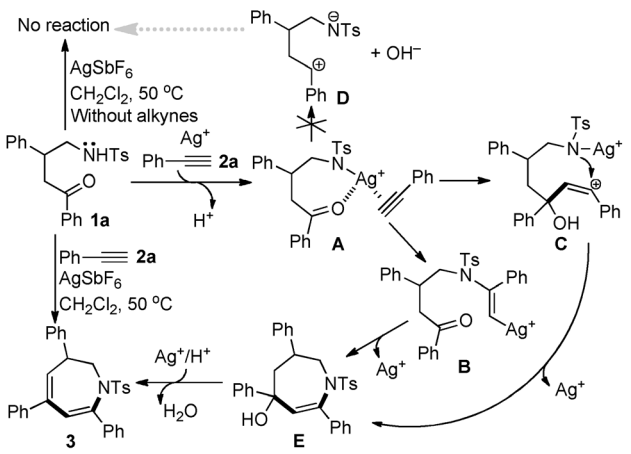
With the optimized conditions in hand, we decided to screen the scope of both γ-amino ketones and alkynes for the [5+2] cycloaddition (Schemes 2 and 3). As shown in Scheme 2, this [5+2] cycloaddition method was found to be applicable to a diverse range of terminal and internal alkynes in the presence of 4-methyl-*N*-(4-oxo-2,4-diphenylbutyl)benzenesulfonamide (**1a**) and $AgSbF_6$. The results demonstrated that several substituents, such as Me, F, Cl, Br, and acetyl, on the aryl ring of the terminal alkyne were well-tolerated (**4**–**11**); moreover, electron-rich arylalkynes were more reactive than electron-deficient arylalkynes. Steric hindrance induced by substituents on the aryl ring only slightly affected the reaction. For example, substrates bearing a Me group at the *para*- or *ortho*-position afforded the corresponding azepines **4** and **8** in 82% and 77% yield, respectively. However, a substrate with a *para*-acetyl group led to a lower yield of azepine **7** (47%). Notably, F, Cl, and Br substituents were compatible with the optimized conditions, thereby facilitating modifications at the halogenated positions (**5**, **6**, and **9**–**11**). Both 1-ethynylnaphthalene and a heterocycle-containing alkyne were viable substrates, which makes this method more useful for the preparation of pharmaceuticals and natural products (**12** and **13**). Using an internal alkyne, however, the reaction gave a low yield (**14**). After a series of experiments, we were pleased to find that satisfactory yields could be obtained from internal alkynes in the presence of $AgSbF_6$, $[\{RhCpCl_2\}_2]$, and $Cu(OAc)_2$; however, instead of the expected azepines, spirocycles **14** and **15** were obtained through sp^2 C–H activation.[10] Unfortunately, aliphatic alkynes are not viable for the current reaction.



Scheme 3. Scope of γ-amino ketones **1**. Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $AgSbF_6$ (15 mol%), and CH_2Cl_2 (2 mL) at 50°C under argon atmosphere for 24–48 h.

We next set out to exploit the scope of γ-amino ketones (Scheme 3). First, the substitution effect at the 2 positon of the γ-amino ketones was examined. The results showed that both functionalized aryl and alkyl groups were compatible with the optimized conditions (**16**–**22**), and that electron-deficient aryl groups lead to a lower reactivity than electron-rich aryl groups. Whereas a *p*-MeC_6H_4 substituted γ-amino ketone furnished the desired azepine **16** in 77% yield, the *p*-$NO_2C_6H_4$-substituted substrate offered the corresponding azepine **19** in 59% yield. A γ-amino ketone bearing two substituents, namely a Ph and a Me group, at the 2 position was also converted into azepine **22** in good yield. Extensive screening revealed that γ-amino ketones bearing substituted aryl groups in the 4 position were compatible with the optimized conditions to react with different alkynes; thus the desired azepines **23**–**26** were smoothly obtained in good yields, and the structure of **25** was unambiguously confirmed by single-crystal X-ray diffraction analysis (see the Supporting Information). Two simple aliphatic γ-amino ketones were found to successfully react with phenylacetylene (**2a**) and $AgSbF_6$, to construct azepines **27** and **28** in 67% and 71% yield, respectively. However, substrates **1** with a *N*-PhCO or a *N*-Me group instead of the *N*-Ts group, show no reactivity under the optimized conditions (**29** and **30**).

The mechanisms outlined in Scheme 4 are proposed on the basis of the results described above, and are supported by data obtained from in situ monitoring of the reaction of **1a** with **2a** by ^{1}H NMR spectroscopy (Supporting Information, Figure S1).[1–4,9,11] Initially, cleavage of the N–H bond in γ-amino ketone **1a** with Ag^+ and complexation with alkyne **2a** afford intermediate **A**; this hypothesis was supported by in situ ^{1}H NMR analysis.[9] Intermediate **A** may then be converted into three intermediates: 1) intermediate **B**, obtained from nucleophilic addition of the amine to alkyne **2a**, 2) intermediate **C**, obtained from electrophilic addition of the carbonyl carbon to alkyne **2a**, and 3) intermediate **D**. The formation of intermediate **D** can be ruled out, as no reaction was observed when γ-amino ketone **1a** was treated with $AgSbF_6$ in the absence of an alkyne. However, we cannot rule out the electrophilic addition of the carbonyl carbon in intermediate **A** to alkyne **2a**.[11c] According to the results presented, intermediate **B** may be easily obtained; an intramolecular cyclization of vinyl–Ag with the carbonyl group results in intermediate **E**, which contains a hydroxyl substituent. Finally, dehydration of intermediate **E** affords the desired azepine **3** with the aid of the Ag catalyst.



Scheme 4. Proposed reaction mechanism.

In summary, we have established a new and efficient method for the synthesis of 2,3-dihydro-1*H*-azepines, through the silver-catalyzed [5+2] cycloaddition of γ-amino ketones with alkynes. This intermolecular [5+2] cycloaddition reaction has a broad substrate scope and allows the formation of four new chemical bonds in one step, leading to seven-membered ring systems through the release of H_2O as the only by-product. Most importantly, the significance of the azepine skeleton as a structural element should render this method attractive for both synthetic and medicinal chemistry, thus paving the way for the synthesis of other complex biologically active heterocyclic systems. Studies on the mechanism and further applications of this silver-catalyzed method in organic synthesis are currently underway in our laboratory.

Experimental Section

Typical experimental procedure for the $AgSbF_6$-catalyzed [5+2] cycloaddition of γ-amino ketones with alkynes: γ-amino ketone **1** (0.2 mmol), alkyne **2** (0.4 mmol), $AgSbF_6$ (15 mol%), and CH_2Cl_2 (2 mL) were added to a Schlenk tube. The tube was then charged with argon, and the reaction mixture was stirred at 50°C for about 24–48 h, until complete consumption of the starting material was observed, as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the

resulting residue was purified by column chromatography on silica gel (7:1 *n*-hexane/ethyl acetate) to afford the desired azepine product.

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