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Gold-catalyzed [4+3]- and [4+2]-annulations of 3-en-1-ynamides with isoxazoles \emph{via} novel 6π -electrocyclizations of 3-azahepta trienyl cations†

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New gold-catalyzed [4+3]-annulations of 3-en-1-ynamides with isoxazoles afford 4H-azepines efficiently; this process involves 6π electrocyclizations of gold-stabilized 3-azaheptatrienyl cations. In the presence of Zn(OTf)₂, the resulting 4H-azepines undergo skeletal rearrangement to furnish substituted pyridine derivatives. We subsequently develop new catalytic [4+2]-annulations between the same 3-en-1-ynamides and isoxazoles to deliver substituted pyridine products using Au(i)/Zn(ii) catalysts. This work reports the first success of the 6π electrocyclizations of heptatrienyl cations that are unprecedented in literature reports.

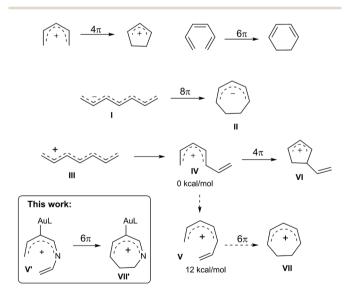
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Introduction

Electrocyclizations of acyclic conjugated π -motifs are powerful tools to access five-, six- and seven-membered carbocycles; prominent examples include Nazarov cyclizations of pentadienyl cations and 6π electrocyclizations of trienes, which have found widespread applications in organic synthesis.

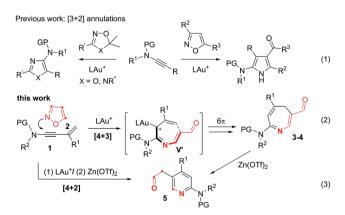


Scheme 1 Electrocyclizations of conjugated π -motifs.

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In the context of seven-carbon π -motifs, heptatrienyl anions I undergo facile 8π electrocyclizations via rapid interconversions among various anion configurations (Scheme 1).⁴ In contrast, heptatrienyl cations III⁵ exclusively undergo Nazarov reactions because of the difficulties of forming all σ -cis configured cations V that have a high energy state.^{5b} 1-Aza- and 1-oxaheptatrienyl cations⁶ were also reported to follow Nazarov cyclizations. The realization of a 6π electrocyclization of conjugated seven-membered cations is formidable but challenging. This work reveals the first success of such seven-membered cyclizations of gold-stabilized 3-azaheptatrienyl cations V' to form azacyclic products 3-4 via a new C-C bond formation.



The advent of gold catalysis has inspired new annulations between alkynes and poor nucleophiles.⁷ N–O containing nucleophiles serve as useful building blocks to construct valuable azacyclic frameworks.⁷ Ye and Hashmi reported interesting [3+2]-annulations of isoxazoles or benzisoxazoles with electron-

rich ynamides, yielding substituted pyrrole derivatives through aza-Nazarov cyclizations of the key intermediate [eqn (1)]. These [3+2]-annulations were extensively expanded to other N–O heterocycles including benzisoxazoles, 1,2,4-oxadiazoles, 1,4,2-dioxazoles and 4,5-dihydro-1,2,4-oxadiazoles, yielding additional five-membered azacycles as depicted in [eqn (1)]. Here, we report two distinct [4+3]- and [4+2]-annulations between 3-en-1-ynamides and isoxazoles using varied catalysts. An Au(ı) catalyst alone delivers 4*H*-azepines 3–4 through 6 π electrocyclizations of intermediates V' [eqn (2)] whereas a combined action of Au(ı)/Zn(ıı) on the same reactants furnishes highly functionalized pyridines 5 [eqn (3)]. With our convenient synthesis, the synthetic utility of new 4*H*-azepines 3–4 is also reported. The synthetic utility of new 4*H*-azepines 3–4 is also reported.

Results and discussion

We examined the reactions of 3-methyl-3-en-1-ynamide ${\bf 1a}$ with 3,5-dimethylisoxazole ${\bf 2a}$ using various gold catalysts. Heating this mixture $({\bf 1a}/{\bf 2a}=1:2 \text{ ratio})$ in hot DCE with 5 mol% LAuCl/AgNTf2 [L = $p(t\text{-Bu})_2(o\text{-biphenyl})$ and IPr] afforded a [4+3]-annulation product, 4H-azepine ${\bf 3a}$, in 64% and 75% yields respectively (Table 1, entries 1–2). Under these conditions, a low loading (1.2 equiv.) of 3,5-dimethylisoxazole ${\bf 2a}$ gave ${\bf 3a}$ in a decreased yield, ${\bf ca}$. 62% (entry 3). With a 10 mol% catalyst, IPrAuCl/AgNTf2 gave a clean reaction, yielding desired ${\bf 3a}$ up to 91% (entry 4). We tested other phosphine ligands such as PPh3 and P(OPh)3, yielding desired ${\bf 3a}$ in satisfactory yields (78–81%, entries 5–6). Other counter anions such as OTf $^-$ and SbF $_6$ $^-$ were also effective in producing ${\bf 3a}$ in 85–88% yields (entries 7–8). AgNTf2 alone was not active at all (entry 9).

Table 1 [4+3]-Annulations over various gold catalysts

		x	Time [h]	Yield ^b [%]		
Entry	Catalyst [mol%]			1a	3a	1a-H'/1a-H"
1 ^c	LAuCl/AgNTf ₂ [5]	2	3	20	64	_
2^d	IPrAuCl/AgNTf ₂ [5]	2	7	12	75	7 [2.5:1]
3	IPrAuCl/AgNTf ₂ [5]	1.2	7	23	62	5 [1:1]
4	IPrAuCl/AgNTf ₂ [10]	2	3	_	91	Trace
5	PPh ₃ AuCl/AgNTf ₂ [10]	2	3.5	_	81	5[1.25:1]
6	[PhO] ₃ PAuCl/AgNTf ₂ [10]	2	3.5	_	78	13[1.1:1]
7	IPrAuCl/AgSbF ₆ [10]	2	2.5	_	85	6[1.4:1]
8	IPrAuCl/AgOTf [10]	2	2	_	88	Trace
9	AgNTf ₂ [10]	2	15	33	_	11

 a [1a] = 0.15 M. b Product yields are reported after separation from a silica column. c L = $p(t\text{-Bu})_2(o\text{-biphenyl})$. d IPr = 1,3-bis(diisopropylphenyl)-imidazol-2-ylidene. Ms = methanesulfonyl, DCE = 1,2-dichloroethane, and Tf = trifluoromethanesulfonyl.

Table 2 [4+3]-Annulations with various 3-en-1-ynamides

 a [1] = 0.15 M. b Product yields are reported after separation from a silica column. EWG = electron withdrawing group.

Table 3 [4+3]-Annulations with various isoxazoles

Entry	(R^1, R^2)	2	Time [h]	Yield [%]	4
(1)	н, н	2b	4	84	4a (X-ray)
				8	7a′
(2)	H, Me	2d	3	75	4b
(3)	Me, H	2c	3	87	4c
(4)	Et, Et	2e	6	85	4d
(5)	<i>n</i> -Bu, <i>n</i> -Bu	2f	7	81	4e
(6)	Me, n-Bu	2g	3	82	4f
(7)	<i>n</i> -Bu, <i>c</i> -Pr	2h	2	77	4g
(8)	Ph, <i>n</i> -Bu	2i	4	69	4h
(9)	Ph, Ph	2j	6.5	61	4i
				30	5i (X-ray)
(10)	Me, Ph	2k	4	71	4j
	Ph O R1 N	N_Ts	R ¹ = Ph (5i) R ¹ = Me (5j)	15	5j

 a [1b] = 0.15 M. b Product yields are reported after separation from a silica column.

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Suitable substituents of 3-en-1-ynamides **1** are crucial to achieve 6π cyclizations of 3-azaheptatrienyl cations **V**' [eqn (2)]. We tested the reactions on 3-en-1-ynes **1b–1m** bearing a C(3)-substituent to circumvent aza-Nazarov cyclizations as reported in Ye's work. Herein, only entries 9 and 10 showed the presence of 3-azanorcaradienes 3'. We examined these [4+3]-annulations on 3-methyl-3-en-1-ynamides **1b–1e** bearing various sulfonamides NTsR⁴ (R⁴ = Me, cyclopropyl, benzyl and N(n-C₄H₉) (-SO₂Bu)), affording the desired 4H-azepines **3b–3e** in high yields (84–90%, Table 2, entries 1–4). Nevertheless, this new annulation becomes less efficient for 3-en-1-ynamide **1f** bearing an oxazolidin-2-one to yield product **3f** in 64% yield (entry 5).

We altered the C(3)-substituents as in substrates **1g-1i**; their resulting products **3g-3h** (\mathbb{R}^1 = isopropyl and cyclopropyl) were obtained in 74-79%, and **3i** (\mathbb{R}^1 = Ph) with only 58% yield (entries 6-8). Notably, when a long *n*-butyl group was present as in species **1j** and **1k**, their corresponding reactions afforded compounds **3j/3j'** = 5/1 and **3k/3k'** = 11.1 : 1, respectively, in 55% and 68% yields (entries 9-10). For *E*-configured trisubstituted 3-en-1-yne **1l** (\mathbb{R}^1 = Me, \mathbb{R}^2 = Ph and \mathbb{R}^3 = H), 4*H*-azepine **3l**

Scheme 2 New functionalization of 4H-azepines.

and pyrrole **6l** were obtained in equal proportions (entry 11). When a cyclohexenyl group was present for alkene as in species **1m**, pyrrole product **6m** was dominant over azepine **3m** (entry 12). Accordingly, preferable 3-en-1-ynes comprise a small R² or R³ substituent whereas R¹ must be substituted. Herein, the structures of 4*H*-azepines **3b** and **3l**, and pyrrole species **6m** were confirmed with X-ray diffraction.¹¹

Isoxazoles of a wide scope are compatible with these [4+3]-annulations, as depicted in Table 3. The reaction of unsubstituted isoxazole $2\mathbf{b}$ with model 3-en-1-ynamide $1\mathbf{b}$ afforded the desired 4H-azepine $4\mathbf{a}$ in 84% yield, together with pyrrole $7\mathbf{a}'$ in only 8% yield (entry 1). Mono-substituted 3-methyl or 5-methyl isoxazoles $2\mathbf{c}$ and $2\mathbf{d}$ are also suitable for these annulations to afford compounds $4\mathbf{b}$ and $4\mathbf{c}$ in 75% and 87% yields, respectively (entries 2–3). We prepared additional 3,5-disubstituted isoxazoles $2\mathbf{e}$ – $2\mathbf{i}$ with \mathbf{R}^1 = alkyl and phenyl, and \mathbf{R}^2 = alkyl; their annulations proceed smoothly to produce desired $4\mathbf{d}$ – $4\mathbf{h}$ in 69–85% yields (entries 4–8). For di-substituted isoxazoles $2\mathbf{j}$ and $2\mathbf{k}$ bearing \mathbf{R}^2 = Ph, 4H-azepines $4\mathbf{i}$ and $4\mathbf{j}$ were obtained in 61% and 71% yields respectively, together with their rearrangement products $5\mathbf{i}$ and $5\mathbf{j}$ in 15–30% yields (entries 9–10). Compounds $4\mathbf{a}$ and $5\mathbf{i}$ were characterized by X-ray diffraction. 11

Our convenient synthesis of 4*H*-azepines provides new synthetic utilities; several new functionalizations are depicted in Scheme 2. NaBH₄-reduction of species 3**b** delivered an alcohol derivative 7**a** in 84% yield. Selective hydrogenation of the same species afforded 2-aza-1,3-dien-5-one 7**b** in 71% yield. A final treatment of 4*H*-azepine 3**b** with NBS in acetone afforded compound 7**c**, of which the molecular structure was determined by ¹H NOE spectra.

The Lewis-catalyzed rearrangement of 4*H*-azepines 3–4 to substituted pyridines 5 [eqn (3)] is unprecedented in 4*H*-azepine chemistry.¹⁰ We undertook such novel [4+2]-annulations

Table 4 [4+2]-Annulations between 3-en-1-ynamides and isoxazoles

Entry	(R^1, R^2, EWG)	1	(R^3, R^4)	2	Time [h]	Yield [%]	5
(1)	Me, Me, Ts	1b	Me, Me	2a	19	73 (35) ^c	5a (X-ray)
(2)	n-Bu, Me, Ts	1k	Me, Me	2a	33	64	5 b
(3)	c-Pr, Me, Ts	1h	Me, Me	2a	20	56	5 c
(4)	<i>i</i> -Pr, Me, Ts	1g	Me, Me	2a	15	51	5 d
(5)	Me, n-Bu, Ms	1a	Me, Me	2a	28	63	5e
(6)	Me, Me, Ts	1b	<i>n</i> -Bu, <i>n</i> -Bu	2f	19	78	5f
(7)	Me, Me, Ts	1b	Et, Et	2e	16	69	5g
(8)	Me, Me, Ts	1b	nBu, c-Pr	2h	20	75	5 h
(9)	Me, Me, Ts	1b	Ph, Ph	2j	24	80	5i (X-ray)
(10)	Me, Me, Ts	1b	Me, Ph	2k	30	75	5j

^a [1] = 0.15 M. ^b Product yields are reported after separation from a silica column. ^c The value in parentheses is reported using a mixture of IPrAuCl/AgNTf₂ (10 mol%) and Zn(OTf)₂ (20 mol%) in hot DCE (70 °C, 48 h); **3b** was also isolated in 28% yield.

Scheme 3 A plausible reaction mechanism.

between 3-en-1-ynamides 1 and isoxazoles 2 using Au(I)/Zn(II) in a relay series, as depicted in Table 4. In the reactions of various 3-substituted 3-en-1-ynamides 1 ($R^1 = methyl, n$ -butyl, cyclopropyl and isopropyl) with 3,5-dimethylisoxazole 2a, substituted pyridines 5a-5d were obtained in satisfactory yields (51-73%, entries 1-4). In entry 1, if the reaction was performed with combined Au(1)/Zn(11) catalysts in a non-relay operation, compounds 5a and 3b were isolated in 35% and 28% yields respectively. For 3-en-1-ynamide 1a bearing a NMs(n-butyl), the corresponding product 5e was obtained in 63% yield (entry 5). We tested the reactions on 3,5-disubstituted isoxazoles 2e-2f & 2h bearing all alkyl substituents, producing desired 5f-5h in good yields (69-78%, entries 6-8). For such disubstituted isoxazoles bearing $R^4 = Ph$, the reactions afforded the desired pyridine derivatives 5i and 5j in 75-80% yields (entries 9-10). The molecular structures of compounds 5a and 5i were characterized by X-ray diffraction.11

Scheme 3 rationalizes the crucial roles of substituents of 3en-1-ynamides in the chemoselectivity that relies on two conformational structures **D** versus **D**'. The N-attack of isoxazole at gold- π -ynamide A is expected to form a gold-carbene D', which can be visualized as a gold-stabilized cycloheptatrienyl cation. Conformation **D** is favorable with R = H, which prefers aza-Nazarov reactions. 12 When a C(3)-substituent is present (R = alkyl and aryl), all σ -cis configured species \mathbf{D}' are the preferable geometry to induce novel 6π electrocyclizations. This ring closure is expected to proceed through an attack of enamide at the alkenylgold moiety that is also visualized as a goldstabilized cation. Additional C(4)-substituents render the formation of cations D' difficult, thus yielding pyrrole 6 as byproducts. A loss of an acidic proton from seven-membered cations E is expected to yield azepines 3-4. 4H-Azepines 3-4 bear an enone conjugated with a triene; this extensive conjugation is very stable to impede a 6π electrocyclization of their triene moieties unless a Lewis acid is present. Zn(OTf)₂ likely coordinates with the carbonyl of 4H-azepine 3 to generate a 2azapentadienyl cation F bearing a zinc enolate, further enabling an intramolecular cyclization to generate species G. A 1,2-acyl shift14 of species G delivers the observed product 5.13

Conclusions

In summary, this work describes new gold-catalyzed [4+3] annulations of 3-substituted 3-en-1-ynamides with isoxazoles to form 4*H*-azepines. A relay catalysis is also developed with Au(1)/Zn(11) catalysts to achieve [4+2] annulations from the same reactants. The mechanisms of gold-catalyzed [4+3] annulations involve unprecedented 6π electrocyclizations of 3-azacycloheptatrienyl cations to form 4*H*-azepines 3–4 efficiently. Control experiments confirm that 4*H*-azepines 3–4 are catalyzed by Zn(OTf)₂ to undergo new rearrangement reactions to form substituted pyridine derivatives.

Conflicts of interest

The authors declare no conflict of interest.

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