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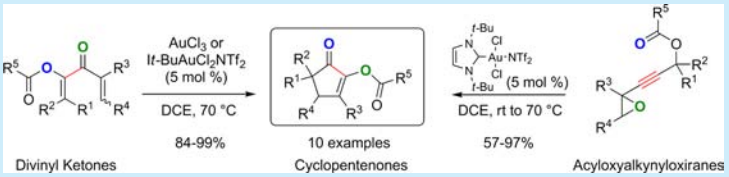
Gold(I)/(III)-Catalyzed Rearrangement of Divinyl Ketones and Acyloxyalkynyloxiranes into Cyclopentenones

Marie Hoffmann,[†] Jean-Marc Weibel,[†] Pierre de Frémont,[‡] Patrick Pale,*[,†] and Aurélien Blanc*[,†]

[†]Laboratoire de Synthèse, Réactivité Organiques et Catalyse and [‡]Laboratoire de Chimie de Coordination, Institut de Chimie, UMR 7177-CNRS, Université de Strasbourg, 4 rue Blaise Pascal, 67070 Strasbourg, France

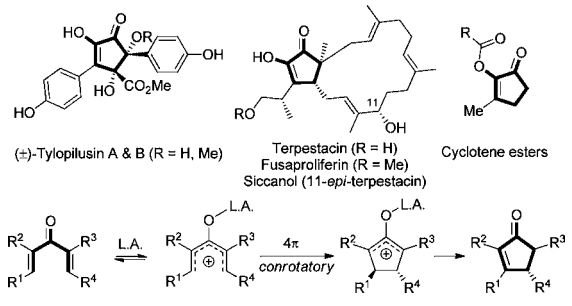
Supporting Information



ABSTRACT: Multifaceted gold(I/III) catalysts with their carbophilic and oxophilic characters catalyzed very efficiently the formation of hydroxylated cyclopentenones from simple divinyl ketones or acyloxyalkynyloxiranes. The Nazarov reaction is rapidly performed in dichloroethane with 5 mol % of the simple gold(III) trichloride salt at 70 °C, while the rearrangement of alkynyloxiranes requires 5 mol % of a more stable NHC gold(III) triflimidate complex.

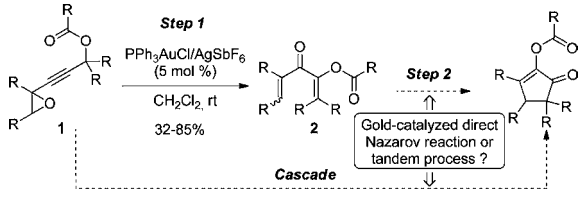
Functionalized five-membered rings, especially hydroxylated cyclopentenones, are important units of numerous natural products, such as the antibiotic tylopilusins[1] isolated from mushrooms or the anti-HIV and anti-angiogenesis terpestacin family[2] (Scheme 1). Such rings are also key building blocks toward various useful compounds, from prostaglandin and related drugs[3] to the cyclotene family[4] of fragrance ingredients (Scheme 1).

Scheme 1. Some Examples of Hydroxylated Cyclopentenone Natural Products and Lewis Acid Catalyzed Nazarov Reaction Toward the Cyclopentenone Motif



As a result of the various interests of hydroxylated cyclopentenones, numerous routes have been developed to achieve their synthesis. Among them, the Nazarov reaction provides unique perspectives due to its stereoselectivity[5] and, of course, has been used as a key step in many natural product syntheses.[6] This reaction required divinyl ketones as substrates and a Lewis acid as catalyst (Scheme 1). Although various Lewis acids have already been used,[7] gold salts or complexes have surprisingly never been explored in the direct cyclization of divinyl ketones.[8] However, it is worth mentioning that some enynyl ketones could give rise to Nazarov products, either as intermediates toward furocyclopentenones or after heterocyclization.[9] Since we previously synthetized acyloxylated divinyl ketones **2** by a gold-catalyzed rearrangement of acyloxypropynyloxiranes **1** (Scheme 2, step 1),[10] we looked for gold-catalyzed conditions able to convert these divinyl ketones to cyclopentenones (Scheme 2, step 2) and then envisaged a one-pot cascade reaction in order to directly obtain five-membered rings from alkynyl epoxides (Scheme 2, cascade). In the present communication, we present our results demonstrating the viability of both the Au-catalyzed Nazarov reaction and the direct conversion of acyloxypropynyloxiranes to cyclopentenones in the presence of appropriate gold catalyst.

Scheme 2. Gold(I)-Catalyzed Rearrangement of Alkynyloxiranes into Divinyl Ketones



To look for the best conditions to produce cyclopentenones from divinylketones, the simple 3-(2,2-dimethylpropionyloxy)-2,5-dimethylhexa-1,4-dien-3-one **2a** was easily prepared in 3 steps including step 1 in Scheme 2 (see Supporting Information) and submitted to various gold catalysts (Table 1). Gold(I) derivatives, even as their electrophilic cationic forms, did not lead to any transformation at room temperature

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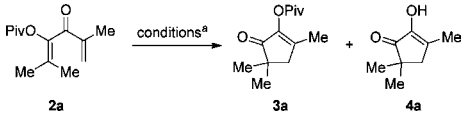
Table 1. Screening of Reaction Conditions for the Au-Catalyzed Transformation of Divinyl Ketone 2a into Cyclopentenones 3a and 4a



2a 3a 4a

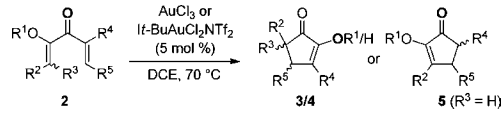
entry	catalyst (5 mol %)	time (h)	cumulative yield (%)	3a:4a (%)
1	$PPh_3AuCl/AgSbF_6$	24[b]	c	c
2	$PPh_3AuCl/AgSbF_6$	0.5	91	14.1/1
3	PPh_3AuNTf_2	6	87	11.4/1
4	$PPh_3AuCl/AgOTf$	4.5	87	3.8/1
5	$L^1AuSbF_6.MeCN$[d]	16	81	5.8/1
6	$L^2AuCl/AgSbF_6$[e]	0.5	92	12.1/1
7	$IPrAuCl/AgSbF_6$	1	98	6/1
8	$AuCl_3$	0.1	97	9.8/1
9	$NaAuCl_4.2H_2O$	2	82	7.2/1
10	$It\text{-}BuAuCl_2NTf_2$	0.75	93	17.6/1
11	$AgSbF_6$	18	85	1.7/1
12		24	c	c

[a]Reactions run under argon at 70 °C in DCE, c = 0.5 mol/L. [b]Reaction run at rt. [c]No conversion. [d]L^1 = JohnPhos. [e]L^2 = tris(2,4-di-*tert*-butylphenyl)phosphite.

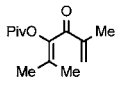
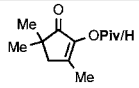
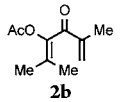
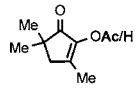
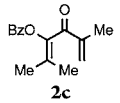
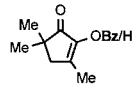
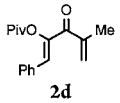
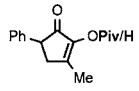
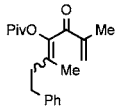
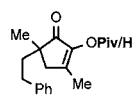
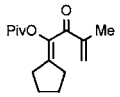
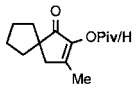
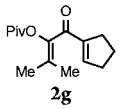
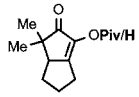
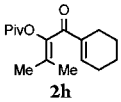
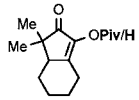
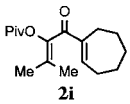
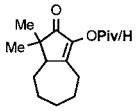
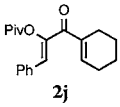
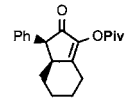
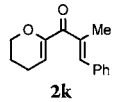
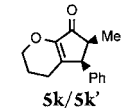
(Table 1, entry 1) but readily produced the expected cyclopentenone in 1,2-dichloroethane at 70 °C in high yields (Table 1, entries 2−7). However, a mixture of the expected 2-pivaloyloxycyclopentenone **3a** and its free form (2-hydroxy) **4a** were isolated. The former was the major one, while the latter could usually be detected only in trace amounts (**3a**/**4a**, 6−15/1), except when silver triflate was used to *in situ* prepare the active catalyst (Table 1, entry 4), suggesting that adventitious water would be responsible for some *in situ* ester hydrolysis. Despite high overall yields, large variation in reaction time was observed, the more electrophilic and bulkier ligands giving the faster reactions (Table 1, entries 2 and 6 vs 3 and 5). Interestingly, NHC-gold(I) complex combined both very high efficiency and high reaction rate (Table 1, entry 7). Not so surprisingly, the more electrophilic gold(III) complexes exhibited higher reactivity, very rapidly giving **3a** in high yields (Table 1, entries 8 and 9). Among them, the simple gold trichloride proved to be the most effective, quantitatively yielding to the cyclized products (Table 1, entry 8). Here also, NHC-gold(III) triflimidate complex[11] exhibited an excellent activity along with a high selectivity in favor of the pivaloylated product **3a** (Table 1, entry 10). Control experiments revealed that silver hexafluoroantimonate could catalyze this reaction, but after long reaction time and with a poor selectivity (Table 1, entry 11), while without catalyst, no transformation occurred (Table 1, entry 12).

With these conditions in hand, the scope of this gold(III)-catalyzed Nazarov reaction was then explored. Various acyloxy divinyl ketones **2b−j** were thus prepared from alkynyloxiranes **1a−j** (see Supporting Information) and submitted to $AuCl_3$ or $It\text{-}BuAuCl_2NTf_2$ in 1,2-dichloroethane at 70 °C (Table 2). We first examined the nature of the ester moiety in order to improve the protected/deprotected ratio (**3**/**4**). As expected, acetoxy and benzoyloxy divinyl ketones **2b** and **2c** gave the corresponding Nazarov products in excellent yields (Table 2, entries 1 vs 2 and 3). Interestingly, an excellent selectivity was obtained from the latter **2c** with a 20 to 1 ratio of products **3c**/**4a**, while a modest selectivity (3.8/1) could be achieved with

Table 2. Scope of Gold(III)-Catalyzed Nazarov Reaction



2 3/4 5 (R^3 = H)

entry	divinyl ketone	cyclopentenones	time (h)	yield[a] (3:4)
1	 **2a**	 **3a/4a**	0.1	97[b] (9.8/1)
2	 **2b**	 **3b/4a**	0.33	87[b] (3.8/1)
3	 **2c**	 **3c/4a**	0.33	85[b] (20/1)
4	 **2d**	 **3d/4d**	0.33	85[b] (6.7/1)
5	 **2e**	 **3e/4e**	1	96[c] (2.6/1)
6	 **2f**	 **3f/4f**	24	84[c] (1.8/1)
7	 **2g**	 **3g/4g**	24	71[c,d] (4.5/1)
8	 **2h**	 **3h/4h**	0.1	86[b] (7.6/1)
9	 **2i**	 **3i/4i**	0.33	87[c] (4.1/1)
10	 **2j**	 **3j/3j'**	0.1	74[c] (>20/1) *dr* 2.1/1[e]
11	 **2k**	 **5k/5k'**	0.1[f]	99[b] *dr* 9/1[e]

[a]Cumulative yield (%). [b]Reaction run with 5 mol % of $AuCl_3$. [c]Reaction run with 5 mol % of $It\text{-}BuAuCl_2NTf_2$. [d]20% of starting material was recovered. [e]Ratio *cis*/*trans*. [f]Reaction run at rt.

the former **2b**, probably reflecting the better resistance toward hydrolysis of these esters. Nevertheless, we kept the migratory pivaloyl group for comparison due to its equal robustness during the cascade reaction (Table 4, entries 1 vs 3). Variation of the substitution in position R^2 and R^3 was then evaluated with substrates **2d−f** (Table 2, entries 1 vs 4−6). Very good

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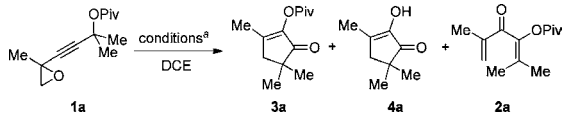
reactivity and yield were maintained switching from dimethyl to Ph/H substituents, but more hindered substituents such as $Ph(CH_2)_2$/Me and particularly cyclopentyl clearly increased the reaction times. In these cases, only the use of I*t*-BuAuCl$_2$NTf$_2$ as catalyst restored the reactivity, leading to high to excellent yields of the corresponding cyclopentenones, but to the detriment of the **3**/**4** ratio (Table 2, entries 5 and 6). It is worth mentioning that spiro cyclopentenones such as **3f**/**4f** could thus be very efficiently obtained. Bicyclopentenone derivatives, motifs occurring in various natural products,[12] could also be prepared from the corresponding cycloalkenyl vinyl ketones **2g**−**i** (Table 2, entries 7−9). Nevertheless, while bicyclo[4.3.0]nonane compounds **3h**/**4h** were nicely formed in standard conditions, substrates **2g** and **2i** required the use of NHC-gold(III) complex to reach full or correct conversions (Table 2, entries 8 vs 7 and 9). The diastereoselectivity of the reaction was further investigated using substrates **2j** and **2k** (Table 2, entries 10 and 11). The dienone **2j** rapidly furnished the cyclopentenone **3j** as mixture of isomers, with only traces of **4j** using I*t*-BuAuCl$_2$NTf$_2$. Despite the 4π conrotatory process, the *cis* isomer was mostly produced, although in a modest ratio (2.1/1), as determined by NOE experiment. Finally, the dihydropyranyl vinyl ketone **2k**, a benchmark substrate for the Nazarov reaction, afforded excellent diastereoisomeric ratio in favor of the *cis* isomer **5k**, as usual for this compound,[13] in a quantitative yield with $AuCl_3$ at room temperature (Table 2, entry 11).

Having demonstrated the direct Au-catalyzed Nazarov reaction from divinyl ketones, we then looked for a one-pot process, starting from acyloxypropynyloxiranes **1** (Cascade in Scheme 2). As already described by us,[10] pivaloylalkynyloxirane **1a** efficiently afforded divinyl ketone **2a**, the transient intermediate in route to cyclopentenones **3a**/**4a**, in the presence of hexafluoroantimonate triphenylphosphinogold(I) complex at room temperature (Table 3, entry 1). Knowing that gold-catalyzed Nazarov reaction required warm conditions, we also evaluated the more stable triflimide gold(I) complex[14] and were pleased to isolate **2a** in slightly better yield (Table 3, entries 2 vs 1). Heating **1a** for 24 h in DCE with Gagosz's or gold trichloride catalysts failed to afford the expected cyclopentenones **3a** or **4a**, and only divinyl ketone **2a** was produced during the reaction (Table 3, entries 3 and 4 vs Table 1, entries 3 and 8). Thinking that degradation of the catalyst could occur during the first step, we conducted the one-pot reaction sequentially by adding another amount of catalyst (5 mol % of PPh_3AuNTf_2 or $AuCl_3$) at 70 °C once **2a** was formed (Table 3, entries 5 and 6). Under such conditions, we successfully obtained cyclopentenones in excellent cumulative yields, although with low selectivity for **3a** vs **4a**. After a large screening of catalysts, we finally found out that only 5 mol % of dichlorotriflimidate I*t*-Bu-gold(III) complex was able to catalyze the cascade reaction in 76% yield (Table 3, entry 7). It is noteworthy that the best ratio of **3a**/**4a** was obtained by forming **2a** at room temperature and then heating the reaction mixture at 70 °C to complete the formation of cyclopentenones (Table 3, entries 7 vs 8).

Having established the optimum reaction conditions (Table 3, entry 7), we next evaluated the scope of this rearrangement on various acyloxyalkynyloxiranes **1a**−**j** (Table 4). Upon gold catalysis, pivaloyl and benzoyl derivatives **1a** and **1c** exhibited the same excellent reactivity and yield, while the acetoxy compound **1b** clearly showed a lack of selectivity and gave modest yield (Table 4, entries 1 and 3 vs 2) presumably due to the less efficient formation of divinyl ketone **2b** (see Supporting Information). We then looked at the influence of R^1 and R^2 substitution on the cascade (Table 4, entries 4−6). As for the Nazarov reaction (Table 2, entries 4−6), compound **1f** underwent the reaction at a considerably slower rate than **1d** and **1e**, but in the all cases good yields have been maintained. Upon cascade conditions, alkynyl epoxides **1g**−**1i** afforded bicyclic systems with even better yields than from divinyl ketones (Table 4, entries 7−9). The stereoselectivity of the cascade was investigated with substrate **1j**. An equal ratio (2.3/

Table 3. Screening of Reaction Conditions for the Tandem Gold-Catalyzed Rearrangement of Acyloxyalkynyloxiranes 1a into Cyclopentenones 3a and 4a

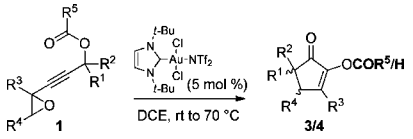


1a 3a 4a 2a

entry	catalyst (5 mol %)	time (h)	temp (°C)	yield[b] (%) (**3a**:**4a**)	yield **2a** (%)
1	PPh_3AuSbF_6	0.33	rt		84
2	PPh_3AuNTf_2	0.33	rt		87
3	PPh_3AuNTf_2	24	rt → 70		62
4	$AuCl_3$	24	rt → 70	trace	57
5	PPh_3AuNTf_2 then + 5 mol %	0.33 1	rt 70	80 (3.2/1)	
6	PPh_3AuNTf_2 then $AuCl_3$	0.33 1	rt 70	87 (4.1/1)	
7	I*t*-BuAuCl$_2$NTf$_2$	2	rt → 70	**76** (**8.5**/**1**)	
8	I*t*-BuAuCl$_2$NTf$_2$	1	70	70 (3.8/1)	

[a]Reactions run under argon in DCE, c = 0.5 mol/L. [b]Cumulative yield.

Table 4. Scope of I*t*-BuAuCl$_2$NTf$_2$-Catalyzed Formation of Cyclopentenones 3:4 from Acyloxyalkynyloxiranes 1



entry		acyloxyalkynylepoxide	products	time (h)	yield[a] (**3**:**4**)
1	**1a**	$R^{1,2,3}$ = Me, R^4 = H, R^5 = *t*-Bu	**3a**/**4a**	2	76 (8.5/1)
2	**1b**	$R^{1,2,3}$ = Me, R^4 = H, R^5 = Me	**3b**/**4a**	2	57 (2.6/1)
3	**1c**	$R^{1,2,3}$ = Me, R^4 = H, R^5 = Ph	**3c**/**4a**	1	75 (8.3/1)
4	**1d**	$R^{1,4}$ = H, R^2 = Ph, R^3 = Me, R^5 = *t*-Bu	**3d**/**4d**	1	74 (3.6/1)
5	**1e**	$R^{1,3}$ = Me, R^2 = $(CH_2)_2$Ph, R^4 = H, R^5 = *t*-Bu	**3e**/**4e**	1.5	78 (1.7/1)
6	**1f**	$R^{1,2}$ = -$(CH_2)_4$-, R^3 = Me, R^4 = H, R^5 = *t*-Bu	**3f**/**4f**	24[b]	71 (1.4/1)
7	**1g**	$R^{1,2}$ = Me, $R^{3,4}$ = -$(CH_2)_3$-, R^5 = *t*-Bu	**3g**/**4g**	2	90 (2.9/1)
8	**1h**	$R^{1,2}$ = Me, $R^{3,4}$ = -$(CH_2)_4$-, R^5 = *t*-Bu	**3h**/**4h**	2.5	89 (8.9/1)
9	**1i**	$R^{1,2}$ = Me, $R^{3,4}$ = -$(CH_2)_5$-, R^5 = *t*-Bu	**3i**/**4i**	2.5	97 (2.6/1)
10	**1j**	R^1 = H, R^2 = Ph, $R^{3,4}$ = -$(CH_2)_5$-, R^5 = *t*-Bu	**3j**/**4j**[c]	1	80 (6.9/1) *dr* 2.3/1[d]

[a]Cumulative yield (%). [b]Reaction started at 70 °C. [c]**4j** isomerized on silica gel into 2-hydroxy-3-phenylcyclopent-2-enone derivative. [d]Ratio of *cis*/*trans* for **3j**/**3j**′ products.

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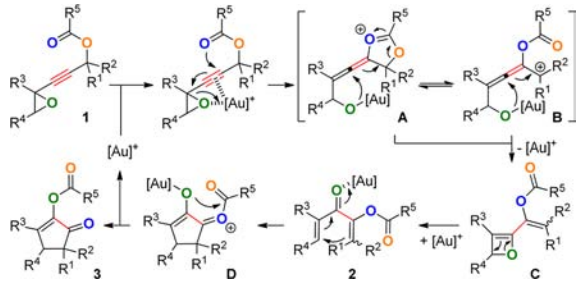
1) to the direct Nazarov reaction (Table 2, entry 10) was observed in favor of the *cis* isomer (Table 4, entry 10). It is noteworthy that for the large majority of substrates, the cascade yield is better than the overall yields of the two independent gold steps.

Based on multifaceted gold catalyst properties, i.e., the ability of gold cations to act as π or σ Lewis acid, the following mechanistic hypothesis could be envisaged for the rearrangement of alkynylepoxides **1** into cyclopentenones **3** via transient divinyl ketone **2** (Scheme 3). As it was previously proposed,

Scheme 3. Mechanistic Hypothesis for Gold-Catalyzed Conversion of Acyloxyalkynyloxiranes 1 into Cyclopentenones 3



intramolecular [1,4]-addition of the acyloxy function via oxophilic or carbophilic Au activations of acyloxyalkynyloxiranes could lead to the formation of the gold allenolate **A**, which is in equilibrium with carbocation form **B**.[15] Both could be trapped by a 4-*exo*-*dig* cyclization, leading to the oxete **C**.[16] Such strained intermediate should rapidly evolved into the divinyl ketone **2** through cycloreversion. The gold-assisted Nazarov reaction favored by electron-donating oxygen at the α-carbon[5d] could next produce the oxocarbenium **D**. The latter could evolve by intramolecular migration of the acyl part furnishing cyclopentenone **3**. The hydroxycyclopentenone **4** could be produced by hydrolysis of intermediate **D**, although in situ deprotection of **3** cannot be excluded.

In conclusion, we have reported for *the first time* that Au(I) or (III) complexes were prone to efficiently catalyze a Nazarov reaction from activated divinyl ketones. Moreover, we also developed a new cascade reaction starting from acyloxyalkynyloxiranes, precursors of divinyl ketones, giving cyclopentenones with excellent yields using an NHC gold(III) triflimide complex. Further works on synthetic applications and an asymmetric version of this Nazarov reaction are in progress in our group.

■ ASSOCIATED CONTENT

Supporting Information

Complete experimental procedures, characterization data, and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ppale@unistra.fr.
*E-mail: ablanc@unistra.fr.

Notes

The authors declare no competing financial interest.

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