Gold-Catalyzed Cyclization of *O*-Propargyl Carbamates under Mild Conditions: A Convenient Access to 4-Alkylidene-2-oxazolidinones

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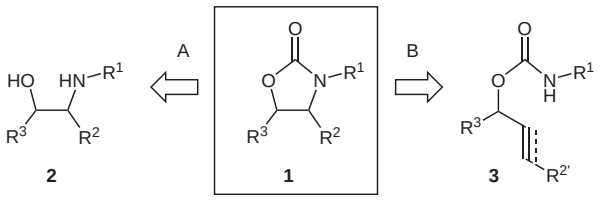
Abstract: On treatment with catalytic amounts of gold(I) chloride (AuCl) and a base co-catalyst, *O*-propargyl carbamates smoothly undergo a 5-*exo-dig* cyclization at room temperature to afford 4-methylene-2-oxazolidinones in high yield. Substrates with a substituent at the alkyne terminus stereoselectively give rise to (*Z*)-4-alkylidene-2-oxazolidinones.

Key words: oxazolidinones, heterocycles, gold catalysis, alkynes

Substituted 2-oxazolidinones (**1**) form a prominent class of heterocyclic compounds because the oxazolidinone substructure occurs in many important pharmaceuticals[1] as well as in prominent chiral auxiliaries and ligands enjoying frequent application in organic synthesis and catalysis.[2]

Following the obvious retrosynthetic disconnection (A; Scheme 1), a variety of convenient methods for the synthesis of 2-oxazolidinones (**1**) from the corresponding amino alcohols (**2**) have been reported (Scheme 1).[2a] An alternative approach (B; Scheme 1), involving a 5-*exo* cyclization of a carbamate precursor of type **3**, is also attractive because it opens, for instance, the possibility to vary substituents in a more modular fashion.



2 1 3

Scheme 1

While such cyclization reactions (**3** → **1**) may proceed through conjugate addition when the multiple bond is activated by an electron-withdrawing group ($R^{2'}$),[3] the transformation of 'unactivated' substrates is also possible,[4] especially through transition-metal-catalyzed intramolecular hydroamination.[5] Thus, the cyclization of *O*-propargyl carbamates of type **4** to 4-methylene-2-oxazolidinones (**5**) can be performed under Cu^{2+} or Ag^+ catalysis (Equation 1).[6] However, rather long reaction times and elevated temperatures are usually required.

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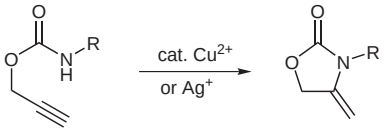
In recent years, gold catalysis[7] has evolved as a powerful concept for addition reactions of nitrogen nucleophiles to alkynes especially in intramolecular cases.[8]

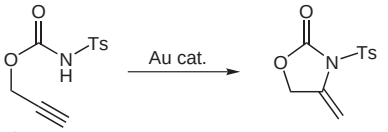


4 5

Equation 1

Herein, we disclose the results of a study demonstrating that gold salts are indeed highly effective catalysts for the cyclization of *O*-propargyl carbamates of type **4**. As such substrates are readily accessible from the corresponding propargylic alcohols and, for instance, an isocyanate (or a carbamoyl chloride), an efficient, flexible and operationally simple route towards 4-alkylidene-2-oxazolidinones was developed.

In a first series of experiments, we investigated the cyclization of the *N*-tosyl carbamate **6**[6] to give the 4-methylene oxazolidinone derivative **7** (Equation 2).



6 7

Equation 2

Using acetonitrile as a solvent and triethylamine (5 mol%) as a base co-catalyst, a number of different gold compounds were initially tested as potential catalysts (5 mol%). The results are summarized in Table 1.

While $Au(PPh_3)Cl$[9] exhibited only little activity, the 'cationic' gold complex $Au(PPh_3)SbF_6$ [generated in situ by addition of $AgSbF_6$ to a $Au(PPh_3)Cl$ solution] afforded the product (**7**) in high yield after one hour at 50 °C. In contrast to $AuSbF_6$, which did not afford the desired product, $AuCl_3$ also showed satisfactory catalytic activity (Table 1, entry 5).[10] Finally, we were delighted to find that simple gold(I) chloride (AuCl) represents a highly efficient catalyst affording **7** in excellent isolated yield (Table 1, entry 6). It is noteworthy that it was possible to perform the reaction under air without any loss of catalytic activity (Table 1, entry 7).

Table 1 Performance of Different Gold Catalysts in the Synthesis of *N*-Tosyl-4-methylene-2-oxazolidinone (**7**) According to Equation 2[a]

Entry	Au catalyst	Temp (°C)	Time (h)	Yield (%)
1	$Au(PPh_3)Cl$	22	1	19
2	$Au(PPh_3)Cl$	50	6	67
3	$Au(PPh_3)SbF_6$	50	1	95
4	$AuSbF_6$	22	1	<5
5	$AuCl_3$	22	6	75
6	AuCl	22	1	97
7[b]	AuCl	22	1	96

[a] Reaction conditions: **6** (0.5 mmol), Au (cat.; 5 mol%), Et_3N (5 mol%) in MeCN (1 mL) under argon.
[b] Reaction was carried out under air.

The combination of a gold catalyst and a base (as a co-catalyst) proved to be essential. In the absence of either of them, no reaction took place at room temperature. Other tertiary amines (5 mol%) such as DABCO, DBU and DMAP as well as potassium *tert*-butoxide were also capable to promote the AuCl-catalyzed cyclization of **6** (Table 2).

Table 2 Influence of the Base Co-catalyst and the Solvent on the AuCl-Catalyzed Cyclization of **6** to **7** According to Equation 2[a]

Entry	Base	Solvent	Time	Yield (%)
1	None	MeCN	1 h	<2[b]
2	Et_3N	MeCN	1 h	97[c]
3	DABCO	MeCN	1 h	>98[b]
4	DBU	MeCN	1 h	91[c]
5	DMAP	MeCN	1 h	83[b]
6	*t*-BuOK	MeCN	1 h	83[b]
7	Et_3N	THF	1 h	91[b]
8	Et_3N	MeOH	1 h	98[b]
9	Et_3N	Toluene	1 h	93[b]
10	Et_3N	CH_2Cl_2	15 min	98[c]
11[d]	Et_3N	CH_2Cl_2	2 h	97[c]

[a] Reaction conditions: **6** (0.5 mmol), AuCl (0.025 mmol), base (0.025 mmol) in solvent (1 mL) at 22 °C under air.
[b] Conversion.
[c] Isolated yield.
[d] Only 0.0025 mmol (0.5 mol%) of catalyst was used.

Besides acetonitrile, other solvents such as toluene, methanol or tetrahydrofuran also proved to be suitable for the cyclization of **6**. In particular, the use of dichloromethane led to enhanced reaction rates and afforded high yields of the product (**7**) after only 15 minutes at room temperature (Table 2, entry 10). Using this solvent it was even possible to decrease the amount of catalyst to 0.5 mol%. However, a two-hour reaction time (room temperature) was required in this case to achieve full conversion.

Having identified efficient conditions for the preparation of **7**, we next investigated whether the AuCl-catalyzed cyclization of *O*-propargyl carbamates is also applicable to the synthesis of differently substituted oxazolidinones. As shown in Table 3 (entry 1), the introduction of substituents at the propargylic position did not decrease the efficiency of the reaction. Thus, starting from the *N*-tosylated substrate **8a**, the spirooxazolidinone **9a** was obtained in a virtually quantitative yield with 5 mol% of AuCl in dichloromethane at room temperature in the presence of triethylamine (5 mol%) as a base (conditions A). The structure of **9a** was unambiguously confirmed by X-ray crystallography (Figure 1).[11]

In contrast to the substrates with a terminal alkyne moiety, the internal alkynes **8b** and **8c** (still carrying a *N*-tosyl substituent) reacted rather slowly. Using acetonitrile as solvent and potassium *tert*-butoxide as base, higher conversions were obtained (conditions B). Still, even at elevated temperatures (conditions C) the conversion never exceeded 60%. Products **9b** and **9c** could be isolated in acceptable yields if one takes into account that the unreacted starting material could be recovered. In a control experiment the most reactive substrates **8a** and **8d** were subjected to the proven cyclization conditions (Table 3, entries 1 and 8) but with omission of the gold catalyst. While no conversion could be detected in the case of **8d** the spirocyclic product **9a** did slowly form from **8a** in a purely base-promoted process (ca. 50% conversion after 1 h). Obviously, this substrate is particularly prone to the cyclization (Thorpe–Ingold effect).

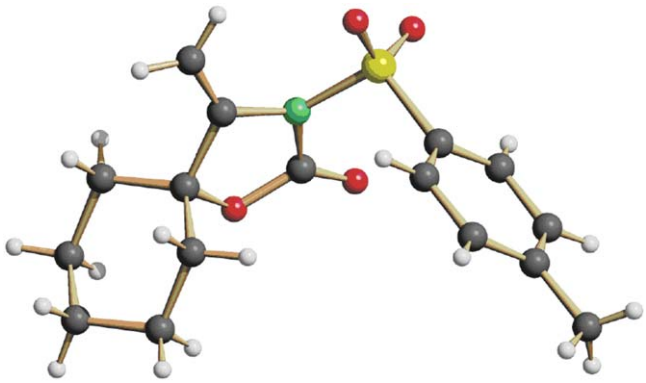
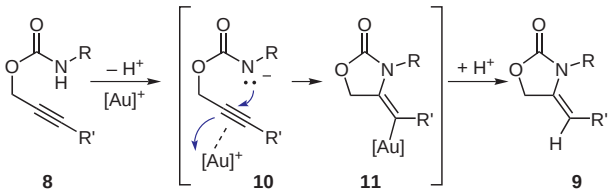


Figure 1 Structure of **9a** in the crystalline state.[11]

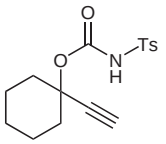
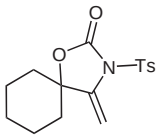
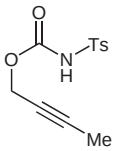
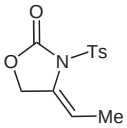
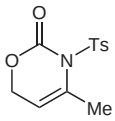
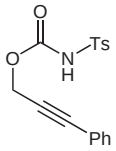
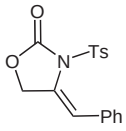
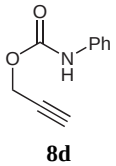
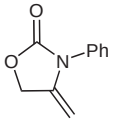
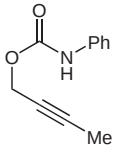
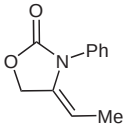
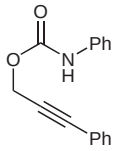
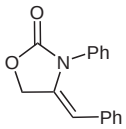
We next investigated substrates with a *N*-phenyl (instead of the *N*-tosyl) substituent (**8d**–**f**). These substrates, which are less acidic, did not react in dichloromethane. However, the terminal alkyne **8d** reacted smoothly in acetonitrile in the presence of triethylamine at room temperature (conditions D), while the internal alkynes again required harsher conditions (conditions C) to afford the expected products in decent (**9e**) to very good (**9f**) isolated yields.

A probable mechanism of the reaction is shown in Scheme 2.[12] It involves a 5-*exo*-*dig* cyclization of an N-nucleophile at the Au-activated alkyne (**10**) with subsequent protolysis of the Au–C bond in the intermediate **11**. Accordingly, it was not unexpected that substrates **8b**, **8c**, **8e** and **8f** (internal alkynes with R′ ≠ H) selectively afforded (within the analytical limits) the *Z*-configured products (**9**), as proven by NOE measurements [irradiation in the signal of the ring-CH_2 protons at about δ = 4.8 (±0.2) ppm].



Scheme 2

Table 3 Results of the Gold-Catalyzed Cyclization of Various Substrates According to Scheme 2[13]

Entry	Substrate	Product(s)	Conditions[a]	Isolated yield[b]
1	 **8a**	 **9a**	A	99%
2	 **8b**	 **9b**	A	<5%
3			B	≤25% (**9b**/*iso*-**9b** = 6:1)
4		 *iso*-**9b**	C	45% (**9b**/*iso*-**9b** = 6:1)
5	 **8c**	 **9c**	A	40%
6			C	51%
7	 **8d**	 **9d**		No conversion
8			A D	99%
9	 **8e**	 **9e**		No conversion
10			A	No conversion
11			B C	52%
12	 **8f**	 **9f**	C	90%[c]

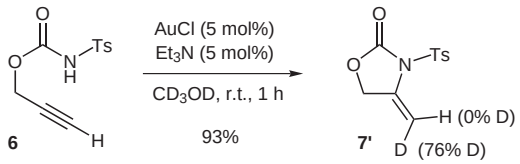
[a] Reaction conditions: A) CH_2Cl_2, AuCl (5 mol%), Et_3N (5 mol%), r.t., 1 h; B) MeCN, AuCl (5 mol%), *t*-BuOK (5 mol%), r.t., 8 h; C) MeCN, AuCl (5 mol%), *t*-BuOK (5 mol%), 60 °C, 6–8 h; D) MeCN, AuCl (5 mol%), Et_3N (5 mol%), r.t., 1 h.

[b] In entries 2–6 and 9–11 the *Z*/*E* selectivity was >98% as determined by ^1H NMR and GC–MS.

[c] In this case, the product was contaminated with about 10% of an isomer (GC–MS), the structure of which was tentatively assigned as the *E* isomer corresponding to **9f**.

It is noteworthy that while most reactions proceeded with virtually perfect regioselectivity and stereoselectivity, a byproduct (*iso*-**9b**) resulting from a 6-*endo* cyclization was formed (to an extent of ca. 17%) only in the case of **9b** (Table 3; entries 3 and 4). In the case of **9f** (see Table 3, entry 12) a byproduct was observed (ca. 10%) which was tentatively assigned as the corresponding *E* isomer. We have no explanation why the selectivity is incomplete in this case; however, we could at least exclude a secondary isomerization of the initially formed *Z*-product **9f** under the reaction conditions.

To probe the proposed mechanism (Scheme 2) and its stereochemical course (*anti* addition to the triple bond), the AuCl-catalyzed cyclization of **6** to **7** was carried out in deuterated methanol (CD_3OD) as a solvent. Indeed, as Equation 3 indicates, deuterium was incorporated only in the *E*-position of the product **7′** as determined by ^1H NMR analysis.



Equation 3

In conclusion, a gold(I)-catalyzed method for the synthesis of 4-alkylidene-2-oxazolidinones has been developed which offers a convenient (and modular) access to a variety of new oxazolidinone derivatives.[14] We are currently investigating applications of this methodology in the synthesis of pharmacologically relevant compounds.

Acknowledgment

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(11) Crystal data for compound **9a**: colorless crystals (from cyclohexane); mp 87–88 °C; $C_{16}H_{19}NO_4S$, FW = 321.10, triclinic, space group P-1; a = 7.2854 (2) Å, b = 8.7222 (3) Å, c = 12.7763 (4) Å; α = 96.866 (2)°, β = 100.075 (2)°, γ = 99.598 (2)°; V = 778.85 (4) Å^3; Z = 2; d_{calc} = 1.370 g/cm^3; R = 0.0391, R_w = 0.0837 for 2517 reflections having I > 2σ(I). Further crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data (CCDC 613241) can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (1223)336033; e-mail: deposit@ccdc.cam.ac.uk].

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(13) **General Procedure for the AuCl-Catalyzed Cyclization of *O*-Propargyl Carbamates**: To a solution of an *O*-propargyl carbamate (**6** or **8a**–**8f**; 0.5 mmol) and a base co-catalyst (0.025 mol, 5 mol%) in solvent (2 mL) was added AuCl (0.025 mol, 5 mol%). The mixture was stirred at r.t. or 60 °C for the time specified in Tables 2 and 3. Conversion was monitored by TLC and/or GLC analyses. The reaction mixture was filtered through a small pad of Celite® (elution with CH_2Cl_2). Removal of the solvent under reduced pressure and purification of the residue by flash chromatography on SiO_2 (cyclohexane–EtOAc, 3:1) afforded the products (**7** or **9**) as colorless oils or solids.
4-Methylene-3-(toluene-4-sulfonyl)-1-oxa-3-azaspiro[4.5]decan-2-one (9a): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34–1.74 (m, 10 H), 2.41 (s, 3 H), 4.39 (d, ^2J = 3 Hz, 1 H, C=CH), 5.46 (d, ^2J = 3 Hz, 1 H, C=CH), 7.31 (d, ^3J = 8.3 Hz, 2 H), 7.89 (d, ^3J = 8.3 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.36 (t), 21.65 (q), 24.28 (t), 36.64 (t), 84.83 (s), 90.14 (t), 127.92 (d), 129.75 (d), 134.31 (s), 144.96 (s), 145.94 (s), 150.26 (s). IR (ATR): 1782 (ss, C=O), 1660 (s, C=C) cm^{-1}. MS (DIP–EI, 70 eV): *m*/*z* (%) = 321 [M$^+$], 166 (14), 155 (24), 105 (12), 94 (23), 91 (100), 81 (16),

65 (33). HRMS (EI): *m*/*z* [M]$^+$ calcd for $^{12}C_{16}H_{19}{}^{14}N^{16}O_4{}^{32}S$: 321.1035; found: 321.104.

(*Z*)-4-Ethylidene-3-tosyloxazolidin-2-one (9b): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.85 (td, ^5J = 1.8 Hz, ^3J = 7.36 Hz, 3 H, CH_3), 2.42 (s, 3 H), 4.62 (app pent, 2 H,), 5.24 (tq, ^4J = 1.8 Hz, ^3J = 7.4 Hz, 1 H), 7.33 (d, ^3J = 8 Hz, 2 H), 7.92 (d, ^3J = 8 Hz, 2 H). Characteristic signals of the minor isomer *iso*-**9b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.56 (dt, ^5J_t = 1 Hz, ^3J_d = 6 Hz, 2 H), 5.43 (tq, ^4J_q = 1 Hz, ^3J_t = 5 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.63 (q), 21.75 (q), 70.14 (t), 112.43 (q), 128.28 (d), 129.87 (d), 135.4 (s), 138.84 (s), 145.77 (s), 153.54 (s, C=O). IR (ATR): 2923 (w, $C=CCH_3$), 1782 (ss, C=O) cm^{-1}. MS (DIP–EI, 70 eV): *m*/*z* (%) = 267 [M$^+$], 155 (34), 112 (11), 95 (32), 91 (100), 65 (23), 57 (44). HRMS (EI): *m*/*z* [M]$^+$ calcd for $^{12}C_{12}H_{13}{}^{14}N^{16}O_4{}^{32}S$: 267.0565; found: 267.056.

(*Z*)-4-Benzylidene-3-(toluene-4-sulfonyl)oxazolidin-2-one (9c): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 4.82 (d, ^4J = 2 Hz, 2 H), 6.15 (t, ^4J = 2 Hz, 1 H), 7.25–7.31 (m, 7 H), 7.68 (d, ^3J = 8.5 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.71 (q), 70.28 (t), 115.87 (d), 127.13 (s), 127.79 (d), 128.48 (d), 128.54 (d), 129.57 (d), 134.49 (s), 134.80 (s), 145.76 (s), 153.90 (s, C=O). IR (ATR): 3058 (w, C=CR), 1788 (ss, C=O) cm^{-1}. MS (DIP–EI, 70 eV): *m*/*z* (%) = 329 [M$^+$], 174 (12), 155 (33), 130 (68), 103 (25), 91 (100), 77 (26), 65 (31), 51 (9). HRMS (EI): *m*/*z* [M]$^+$ calcd for $^{12}C_{17}H_{15}{}^{14}N^{16}O_4{}^{32}S$: 321.0721; found: 321.072.

4-Methylene-3-phenyloxazolidin-2-one (9d): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.12 (d, ^2J = 2.5 Hz, 1 H, C=CH), 4.21 (d, ^2J = 2.5 Hz, 1 H, C=CH), 5.01 (t, ^2J = 2 Hz, 2 H), 7.30–7.46 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 67.10 (t), 82.00 (t), 126.91 (d), 128.94 (d), 129.15 (d), 133.55 (s), 141.72 (s), 155.97 (s, C=O). IR (ATR): 1757 (ss, C=O), 1680 (s, C=CH) cm^{-1}. MS (DIP–EI, 70 eV): *m*/*z* (%) = 175 [M$^+$], 130 (100), 103 (56), 91 (8), 77 (68), 63 (10), 51 (46). HRMS (EI): *m*/*z* [M]$^+$ calcd for $^{12}C_{10}H_9{}^{14}N^{16}O_2$: 175.0633; found: 175.063.

(*Z*)-4-Ethylidene-3-phenyloxazolidin-2-one (9e): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06 (td, ^5J = 2.3 Hz, ^3J = 7.3 Hz, 3 H), 4.47 (tq, ^4J = 2.3 Hz, ^3J = 7.3 Hz, 1 H), 4.91 (m, 2 H), 7.30–7.43 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.43 (q), 66.06 (t), 93.17 (d), 127.09 (d), 127.17 (d), 128.21 (d), 128.59 (d), 129.55 (d), 129.87 (d), 130.59 (s), 135.16 (s). IR (ATR): 1771 (ss, C=O), 1699 (s, C=CH) cm^{-1}. MS (DIP–EI, 70 eV): *m*/*z* (%) = 207 [M$^+$], 189 (32), 149 (33), 132 (36), 119 (100), 104 (27), 91 (29), 84 (74), 77 (69), 57 (77), 49 (94). HRMS (EI): *m*/*z* [M]$^+$ calcd for $^{12}C_{11}H_{11}{}^{14}N^{16}O_2$: 189.079; found: 189.079.

(*Z*)-4-Benzylidene-3-phenyloxazolidin-2-one (9f): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.10 (d, ^4J = 2.1 Hz, 2 H), 5.67 (s, 1 H), 6.63 (d, *J* = 1.7 Hz, 2 H), 6.81–6.90 (m, 3 H), 6.98–7.06 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.03 (t), 99.89 (t), 125.88 (d), 126.96 (d), 128.12 (d), 128.16 (d), 128.68 (d), 129.74 (d), 132.27 (s), 132.83 (s), 134.60 (s), 156.95 (s, C=O). IR (ATR): 3053 (w, C=CR), 1769 (ss, C=O) cm^{-1}. MS (DIP–EI, 70 eV): *m*/*z* (%) = 251 [M$^+$], 206 (23), 104 (100), 89 (9), 77 (32), 63 (8), 51 (22). HRMS (EI): *m*/*z* [M]$^+$ calcd for $^{12}C_{16}H_{13}{}^{14}N^{16}O_2$: 251.0946; found: 251.094.

(14) During the preparation of this manuscript, a method for the gold-catalyzed synthesis of (isomeric) 3-alkylidene-2-oxazolidinones was reported, which nicely complements the work described here: Robles-Machin, R.; Adrio, J.; Carretero, J. C. *J. Org. Chem.* **2006**, *71*, 5023.