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Gold(I) Catalysis: Selective Synthesis of Six- or Seven-Membered Heterocycles from Epoxy Alkynes

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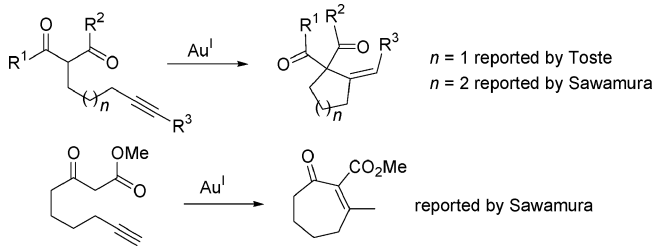
Keywords: Gold / Alkynes / Domino reactions / Heterocycles / Isomerization

Gold(I)-catalyzed intramolecular cycloisomerization of ketone-substituted epoxides with alkynes to six- or seven-membered heterocyclic compounds is firstly introduced in this paper. This procedure involves a cascade isomerization of the ketone-substituted epoxides into 1,3-diketones in the presence of a Lewis acid and subsequent gold(I)-catalyzed selective intramolecular addition of an oxygen or a carbon nucleophile to the alkynes.

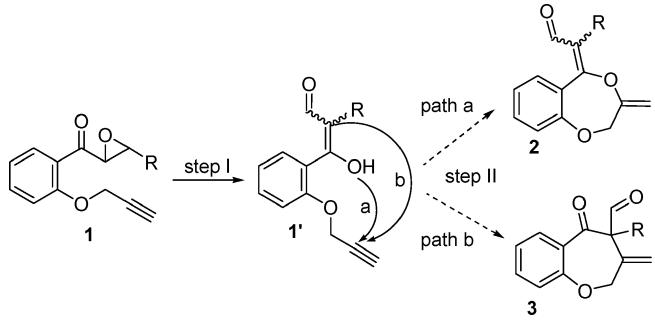
Introduction

Six- and seven-membered oxygen-containing heterocycles are abundant in nature and have attracted much synthetic interest in recent years because of their diverse and important biological properties.[1] Among them, the addition of 1,3-diketones to alkynes plays an important role in organic chemistry. For example, In-,[2] Pd-,[3] and Zn[4]-catalyzed transformations have been well documented before. Toste[5] and co-workers have reported an efficient gold-catalyzed intramolecular addition of β-keto esters to inactivated alkynes, providing the cyclization products derived from the carbon nucleophiles. Later on, Sawamura[6] also reported a similar reaction assisted by "holey phosphines" to give six- or seven-membered rings (Scheme 1). Moreover, some other groups have also reported the nucleophilic addition of 1,3-dicarbonyl compounds to propargyl carboxylates and unactivated olefins catalyzed by gold to give the adducts in good yields.[7] All of these gold-catalyzed reactions have the same feature that the 1,3-diketones act as carbon nucleophiles. Herein, we wish to introduce another new reaction catalyzed by gold to produce six- and seven-membered heterocyclic compounds, in which the alkynes are attacked by 1,3-diketones acting as carbon or oxygen nucleophiles selectively, depending on the employed substrates.

It is well known that cyclizations of epoxy alkynes have provided rapid access to complex structures in easy one-pot processes.[8] Moreover, gold as an effective catalyst to promote the isomerization of epoxy alkynes has been extensively reported recently.[9] In the context of our ongoing efforts to develop cascade reactions using epoxy alkynes as substrates,[10] we envisaged that ketone-substituted epoxides **1** in the presence of acid might undergo isomerization to give 1,3-diketones **1′** (Scheme 2, step I). Subsequent cyclization could occur by two pathways involving either (1) addition of an oxygen nucleophile to the alkyne to afford **2** (Scheme 2, step II, path a) or (2) addition of a carbon nucleophile to the alkyne to afford **3** (Scheme 2, step II, path b), which was similar to the results reported by Toste and Sawamura (Scheme 1).



Scheme 1. Previous examples of Au^I-catalyzed carbocyclization of β-keto esters with alkynes.



Scheme 2. Hypotheses for the one-pot conversion of epoxy alkynes **1** to seven-membered heterocycles.

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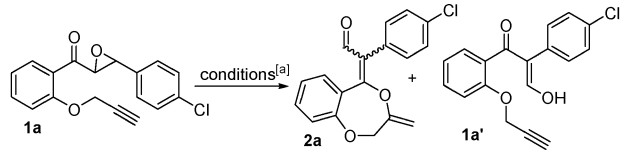
Results and Discussion

To probe these hypotheses, we initially started our investigation by using 0.3 mmol of substrate **1a** and 5 mol-% of $Au(PPh_3)Cl/AgOTf$ in CH_2Cl_2 at room temperature. To our disappointment, although the reaction gave a small amount of **2a** on the basis of ^1H NMR spectroscopy, the product could not be cleanly separated from some unidentified by-products (Table 1, Entry 1). After 30 min at 40 °C **1a** was consumed completely upon treatment with 10 mol-% of $Yb(OTf)_3$. Then, 5 mol-% of $Au(PPh_3)Cl/AgOTf$ was further added at room temperature (20 °C). After 36 h, we found that (*E*)-**2a** and (*Z*)-**2a** were obtained in 36 and 16% yield, respectively (Table 1, Entry 2), along with some impurities (see the Supporting Information). The structure of (*E*)-**2a** was unambiguously determined by X-ray diffraction.[11] By increasing the reaction temperature to 60 °C in the first step, the overall yield of (*E*)-**2a** and (*Z*)-**2a** became slightly lower (Table 1, Entry 3). Changing $Yb(OTf)_3$ to $Sc(OTf)_3$ or $In(OTf)_3$ afforded **2a** in lower yields (Table 1, Entries 4 and 5). By using Brønsted acids such as trifluoromethanesulfonic acid (HOTf) as a cocatalyst to the reaction, complex product mixtures were obtained (Table 1, Entry 6). Switching the CH_2Cl_2 solvent to CH_3NO_2 gave the best result, affording (*E*)-**2a** in 46% yield and (*Z*)-**2a** in 14% yield, respectively (Table 1, Entry 7). Subsequently, the use of $Yb(OTf)_3$ as the sole catalyst afforded **1a′** in 74% yield as a sole product (Table 1, Entry 8). Therefore, we believe the use of $Yb(OTf)_3$ as the Lewis acid was beneficial to promote the rearrangement of oxiranes to form 1,3-diketones.

Table 1. Screening of reaction conditions for the transformation of **1a** into a seven-membered heterocycle.

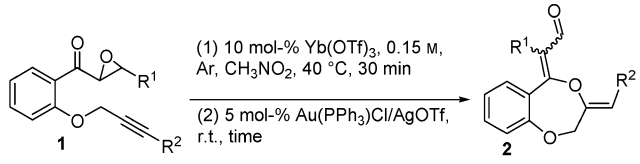


Entry	Conditions	Yield [%][b] (*E*)-**2a**	(*Z*)-**2a**	**1a'**
1	$Au(PPh_3)Cl/AgOTf$ (5 mol-%), CH_2Cl_2, r.t., 36 h		–[c]	
2	(1) $Yb(OTf)_3$ (10 mol-%), CH_2Cl_2, 40 °C, 30 min (2) $Au(PPh_3)Cl/AgOTf$ (5 mol-%), r.t., 36 h	36	16	–
3	(1) $Yb(OTf)_3$ (10 mol-%), CH_2Cl_2, 60 °C, 30 min (2) $Au(PPh_3)Cl/AgOTf$ (5 mol-%), r.t., 36 h	36	10	–
4	(1) $Sc(OTf)_3$ (10 mol-%), CH_2Cl_2, 40 °C, 30 min (2) $Au(PPh_3)Cl/AgOTf$ (5 mol-%), r.t., 36 h	19	10	–
5	(1) $In(OTf)_3$ (10 mol-%), CH_2Cl_2, 40 °C, 30 min (2) $Au(PPh_3)Cl/AgOTf$ (5 mol %), r.t., 36 h	30	9	–
6	(1) HOTf (10 mol-%), CH_2Cl_2, r.t., 30 min (2) $Au(PPh_3)Cl/AgOTf$ (5 mol %), r.t., 12 h		–[c]	
7	(1) $Yb(OTf)_3$ (10 mol-%), CH_3NO_2, 40 °C, 30 min (2) $Au(PPh_3)Cl/AgOTf$ (5 mol-%), r.t., 24 h	46	14	–
8	$Yb(OTf)_3$ (10 mol-%), CH_3NO_2, 40 °C, 30 min	–	–	74

[a] The concentration of substrate was 0.15 M. [b] Isolated yield. [c] Complex reaction mixture.

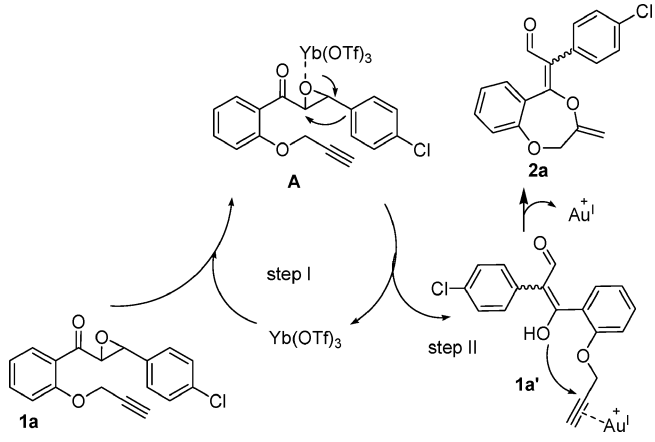
With the optimized reaction conditions in hand, the scope of this one-pot, two-step reaction was then examined as depicted in Table 2. By examining the influence of the R^1 substituents on the benzene rings we found that substrates bearing electron-donating groups (Me, OMe) or electron-withdrawing ones (F, Cl, Br) were smoothly transformed into products **2** in moderate yields (Table 2, Entries 1–5). However, when R^1 was *p*-$NO_2C_6H_4$ or the pyridyl group, no reaction occurred, presumably as a result of the difficult 1,2-aryl transfer of the strongly electron-deficient aromatic ring in the presence of a Lewis acid, as shown in step I of Scheme 3 (Table 2, Entries 6 and 7).[12] Upon further exploring the applicability of this one-pot cycloisomerization to epoxy alkyne **1i** bearing a Br atom at the terminus of the alkyne, we found that the reaction also proceeded smoothly to give products (*E*)-**2i** and (*Z*)-**2i** in 28 and 18% yield, respectively (Table 2, Entry 8).

Table 2. The scope of $Yb(OTf)_3$ and gold(I) cocatalyzed cycloisomerization.



Entry	R^1/R^2	Time [h]	Yield [%][a] *E*-**2**	Yield [%][b] *Z*-**2**
1	*p*-MeC_6H_4/H	24	(*E*)-**2b**: 35	(*Z*)-**2b**: 5
2[c]	*m*-$MeOC_6H_4$/H	24	(*E*)-**2c**: 36 (23)[d]	(*Z*)-**2c**: 12 (7)[d]
3	*p*-FC_6H_4/H	25	(*E*)-**2d**: 43	(*Z*)-**2d**: 18
4	*p*-BrC_6H_4/H	28	(*E*)-**2e**: 44	(*Z*)-**2e**: 12
5	*o*-ClC_6H_4/H	28	(*E*)-**2f**: 42	(*Z*)-**2f**: 14
6	*p*-$NO_2C_6H_4$/H	26	–	–
7	pyridyl/H	26	–	–
8	*p*-FC_6H_4/Br	34	(*E*)-**2i**: 28	(*Z*)-**2i**: 18

[a] Isolated yield. [b] Isolated yield, but containing a trace amount of the corresponding (*E*)-**2**. [c] Some unidentified impurities could not be separated from (*Z*)-**2c**. [d] Distilled CH_3NO_2 was not further dried with 4 Å MS.



Scheme 3. Proposed mechanism for the formation of seven-membered heterocycles.

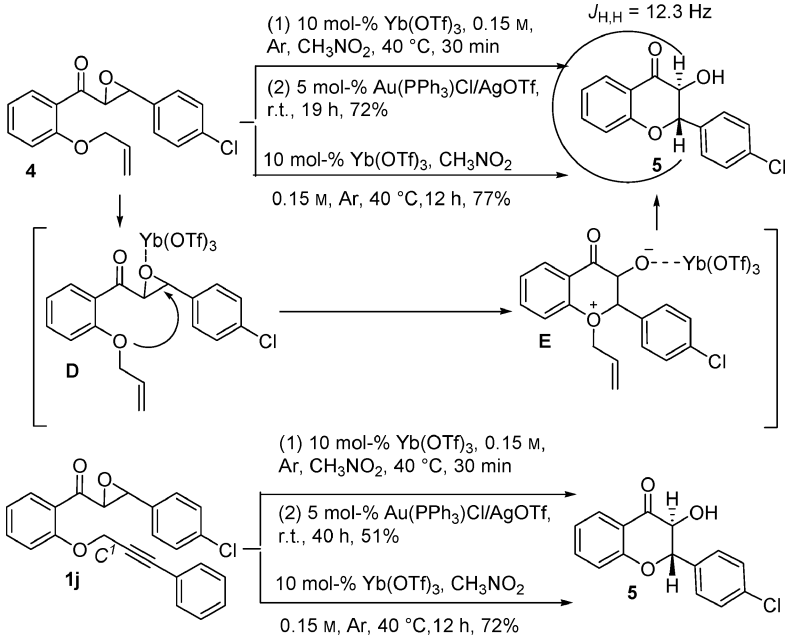
On the basis of the above observations, a plausible mechanism for the formation of the seven-membered heterocycles is proposed in Scheme 3. In step I, the coordination of $Yb(OTf)_3$ to the epoxy moiety of **1a** affords complex **A**. Subsequent 1,2-transfer of the aryl group leads to intermediate **1a′**. In the second step, unlike the results involving carbon nucleophilic addition reported by Toste and Sawamura, the addition of an oxygen nucleophile to the alkyne moiety takes place by adding a gold catalyst to the system, resulting in the formation of products (*E*)-**2a** and (*Z*)-**2a**. In comparison to the example reported by Sawamura, it is conceivable that the two aryl groups in 1,3-diketones would promote the enolization of **1a′**, which might be the driving force for the addition of the oxygen nucleophile to the alkyne moiety.

In addition to epoxy alkynes, epoxy alkene **4** was also examined to obtain the corresponding seven-membered heterocycle, which would be formed by nucleophilic addition of the resulting 1,3-diketone to the double bond cocatalyzed by $Yb(OTf)_3$ and gold(I). However, the reaction did not proceed in accordance with our expectation, and it was found that only product **5** was formed in 72% yield. By further examination of the role of the catalysts, we found that addition of 10 mol-% of $Yb(OTf)_3$ to a solution of **4** in dry CH_3NO_2 resulted in the transformation of substrate **4** into product **5** in 77% yield within 12 h (Scheme 4). Moreover, substrate **1j** could also be transformed into **5** under the similar conditions. This might be due to the fact that an aryl group at the end of the alkyne would weaken the C^1–O bond and increase the nucleophilicity of the oxygen atom, as it would be more negatively charged. Moreover, the phenyl substituent stabilized the propargyl carbocation that is eliminated in the transformation.[7a] Therefore, the intramolecular nucleophilic ring opening of oxirane can take place prior to its rearrangement (Scheme 4).

Inspired by the above results, we next examined the possibility of the reaction by using epoxy alkynes **6** under identical conditions. Unexpectedly, it was found that the use of **6a** as the starting material gave product **7a** in 65% yield, resulting from carbon nucleophilic addition to the alkyne, along with the formation of byproduct **9a** in 13% yield (Table 3, Entry 1).[13] Further systematic screening of the catalysts and solvents revealed that $Au(PPh_3)Cl/AgOTf$ was the best catalyst and CH_2Cl_2 was the best solvent for the reaction (Table 3, Entry 7). It should be mentioned that in toluene, 1,3-diketone **8** was obtained as the major product (Table 3, Entry 5).

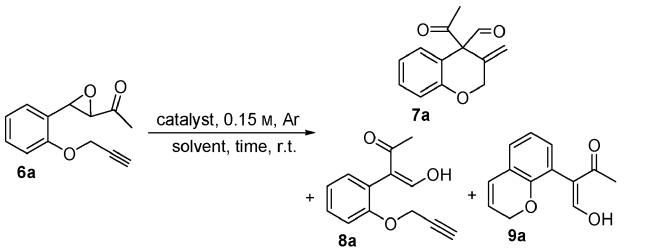
The scope of this reaction was also explored. When R was C_6H_5, β-naphthyl, and *p*-ClC_6H_4, desired products **7** were obtained in moderate yield along with minor products **9** (Table 4, Entries 1–3). However, when R was *o*-$CH_3C_6H_4$, **9e** was obtained as the major product in 47% yield, presumably as a result of the electron-donating group on the benzene ring, which would increase the electronic density of the aryl group, resulting in the formation of product **9e** in a much easier way (Table 4, Entry 4). The yield of **7a** (77%) was higher than those of **7b**–**e** (13–52%), indicating that the aryl group would promote the enolization of intermediate **8** more easily (Scheme 5), which was beneficial to the intramolecular addition of 1,3-diketones to alkynes.

To gain some insight into the mechanism, a control experiment was carried out by subjecting isolated **8a** under the catalysis of $Au(PPh_3)Cl/AgOTf$ (5 mol-%) in dichloromethane. It was found that **7a** and **9a** were obtained in 82 and 9% yield, respectively. On the basis of this control experiment, a proposed mechanism was shown in Scheme 5. Being similar to the mechanism described in Scheme 3, in the presence of gold complex, **6a** easily rearranges into 1,3-diketone **8a** through intermediate **F**. Subsequent addition of a carbon nucleophile to the alkyne–gold complex produces



Scheme 4. Cycloisomerization of **4** or **1j**.

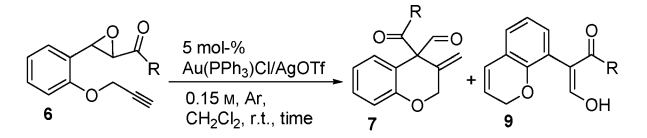
Table 3. Screening of the reaction conditions for the transformation of **6a**.



Entry	Catalyst (3 mol-%)	Solvent	Time [h]	Yield [%][a] 7a	Yield [%][a] 8a	Yield [%][a] 9a
1[b]	(1) $Yb(OTf)_3$ (2) $Au(PPh_3)Cl/AgOTf$	$MeNO_2$	12	65	0	13
2	$Au(PPh_3)Cl/AgSbF_6$	CH_2Cl_2	19	57	0	28
3	$Au(PPh_3)Cl/AgOTf$	CH_2Cl_2	36	74	0	9
4[c]	$AuCl_3$	MeCN	60	0	0	9
5	$Au(PPh_3)Cl/AgOTf$	toluene	48	0	69	0
6	$Au(PPh_3)Cl/AgOTf$	$MeNO_2$	43		complexes	
7[d]	$Au(PPh_3)Cl/AgOTf$	CH_2Cl_2	48	77	0	8

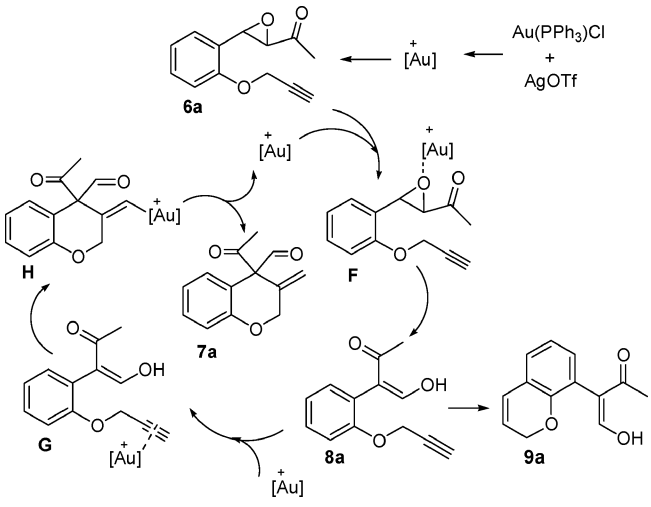
[a] Isolated yield. [b] 10 mol-% of $Yb(OTf)_3$ was added firstly at 40 °C, and after 30 min, 5 mol-% of $Au(PPh_3)Cl/AgOTf$ was added further. [c] 61% of **6a** was recovered. [d] 5 mol-% of catalyst was used.

Table 4. The scope of the reaction for the synthesis of **7**.



Entry	R	Time [h]	Product yield [%][a]	
1	C_6H_5	48	**7b**: 52	**9b**: 26
2	β-naphthyl	48	**7c**: 50	**9c**: 17
3	*p*-ClC_6H_4	48	**7d**: 51	**9d**: 24
4	*o*-MeC_6H_4	48	**7e**: 13	**9e**: 47

[a] Isolated yield and the ratio of **7** and **9** was determined by ^1H NMR spectroscopy.



Scheme 5. Proposed pathway for the formation of six-membered heterocycles.

six-membered product **7a** via intermediates **G** and **H** (Scheme 5).[14]

Conclusions

In summary, we have developed a novel synthetic approach to six- and seven-membered heterocycles from epoxy alkynes catalyzed by gold(I) or $Yb(OTf)_3$/gold(I) in a mild and efficient way through selective carbon or oxygen nucleophilic addition to alkynes. Further investigation on the scope and limitations of this reaction is in progress in our lab.

Experimental Section

General Remarks: Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively. Mass and HRMS spectra were recorded by EI methods. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

Procedure for the Preparation of 2a: To a solution of [3-(4-chlorophenyl)oxiran-2-yl][2-(prop-2-ynyloxy)phenyl]methanone (**1a**; 93.6 mg, 0.3 mmol) in freshly distilled nitromethane (2.0 mL) at 40 °C was added $Yb(OTf)_3$ (0.03 mmol) under an atmosphere of argon for about 30 min. Then, $Au(Ph_3P)Cl$ (0.015 mmol) and AgOTf (0.015 mmol) were added. The reaction mixture was monitored by TLC. When the reaction was complete, the mixture was diluted with EtOAc and evaporated under reduced pressure, and the residue was purified by flash column chromatography (EtOAc/petroleum ether, 1:30). Compound **2a** (56.2 mg) was isolated in 60% yield.

(2*E*)-(4-chlorophenyl)(3-methylene-2,3-dihydro-5*H*-1,4-benzodioxepin-5-ylidene)acetaldehyde [(*E*)-2a]: Yield: 43.1 mg (46%). White solid. M.p. 139–141 °C. IR (NaCl): $\tilde{\nu}$ = 3064, 2927, 2861, 2757, 1664, 1590, 1492, 1321, 1230, 1114 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 4.80 (s, 2 H), 4.80 (s, 1 H), 4.93 (s, 1 H), 7.14–7.26 (m, 2 H), 7.32–7.43 (m, 5 H), 7.50–7.55 (m, 1 H), 9.57 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 74.4, 106.0, 121.5, 122.4, 123.6, 123.7, 128.2, 130.1, 131.9, 133.46, 133.52, 134.1, 152.5, 155.8, 170.0, 191.0 ppm. MS (EI): *m*/*z* (%) = 89 (16.3) [M^+ – 223], 165 (31.4) [M^+ – 147], 228 (27.9) [M^+ – 84], 273 (24.9) [M^+ – 39], 312 (100.0) [M^+], 314 (34.5) [M^+ + 2]. HRMS: calcd. for $C_{18}H_{13}ClO_3$ 312.0553; found 312.0550.

Supporting Information (see footnote on the first page of this article): Detailed procedure and characterization data for the starting materials and products.

Acknowledgments

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[11] CCDC-703815 [for (*E*)-**2a**] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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