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Chemoselective C–C Bond Cleavage of Epoxide Motifs: Gold(I)-Catalyzed Diastereoselective [4+3] Cycloadditions of 1-(1-Alkynyl)oxiranyl Ketones and Nitrones

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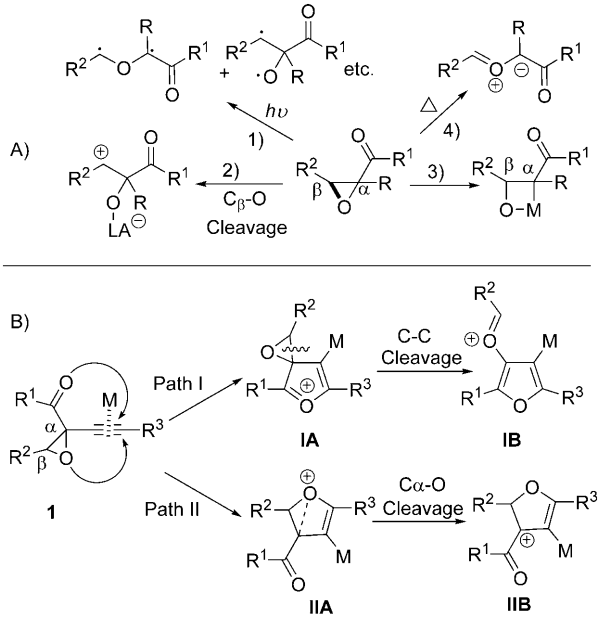
In memory of Professor Xian Huang

Epoxides are highly versatile intermediates in organic synthesis due to their easy access and their susceptibility to ring opening by facile C–O bond cleavage.[1] Despite the fact that the C–O bond cleavage has been extensively studied in organic synthesis, C–C bond cleavage is rarely reported and has limited applications in synthesis due to the harsh conditions required. α,β-Epoxy ketones are an important class of compounds with high synthetic utility and potential for further functionalization. Several ring-opening pathways for α,β-epoxy ketones under different conditions have been demonstrated (Scheme 1 A): 1) photoinduced homocleavage of the epoxide ring to generate a biradical, which can undergo further transformations;[2] 2) Lewis acid mediated C_β–O bond cleavage to produce a zwitterionic intermediate,[3] which can react further with nucleophiles to afford various ketones, or (when R is hydrogen) formation of α-diketones through hydrogen migration; 3) transition-metal-mediated oxidative addition to the C_α–O bond to give a metallaoxetane[4] and subsequent rearrangement to afford 1,3-diketones; 4) C_α–C_β bond cleavage at high temperatures to afford carbonyl ylide intermediates, which can be further applied in 1,3-dipolar cycloadditions.[5–7] Huisgen and March demonstrated that the [3+2] cycloaddition of aldehydes to



Scheme 1. Previously reported ring-opening models of epoxy ketones (A) and our working hypothesis (B).

3-phenyloxirane-2,2-dicarboxylate (with two activating groups) still required 10 days at 125 °C to achieve a satisfactory conversion.[6] The development of new strategies to accomplish the C–C bond cleavage of epoxides under mild conditions are clearly highly desirable. Herein, we report a novel strategy to achieve the C–C bond cleavage of the epoxide ring by introducing an alkyne that can be activated by a carbophilic gold(I) complex. To the best of our knowledge, this is the first example of a metal-catalyzed, selective C–C bond cleavage of epoxy ketones.

It is believed that α,β-epoxy ketones readily undergo C–O bond cleavage rather than C–C bond cleavage due to the preference of coordination of the oxygen atom by the oxo-

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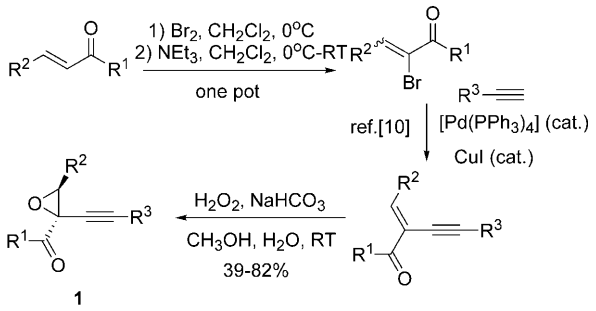
philic Lewis acid to make the C–O bond more labile (Scheme 1A, route 2). Thus, if there were a way to circumvent this binding and activate the epoxide ring by binding the side chain, C–C bond cleavage might be realized.

Encouraged by previous reports,[8] we envisaged that this issue could be addressed by introducing an alkyne to the α position of α,β-epoxy ketones, that is, 1-(1-alkynyl)oxiranyl ketones **1** (Scheme 1B). There are two different reaction pathways in the presence of a carbophilic transition metal or a Lewis acid. Path I shows the carbonyl oxygen attacking the metal-activated alkyne to mediate a heterocyclization to produce intermediate **IA**, which upon further aromatization through C–C bond cleavage affords the furanyl intermediate **IB**. Alternatively, the oxygen atom of the epoxy can attack the metal-activated alkyne (path II) to mediate a heterocyclization and subsequent C_α–O cleavage of intermediate **IIA** will generate intermediate **IIB**.[9]

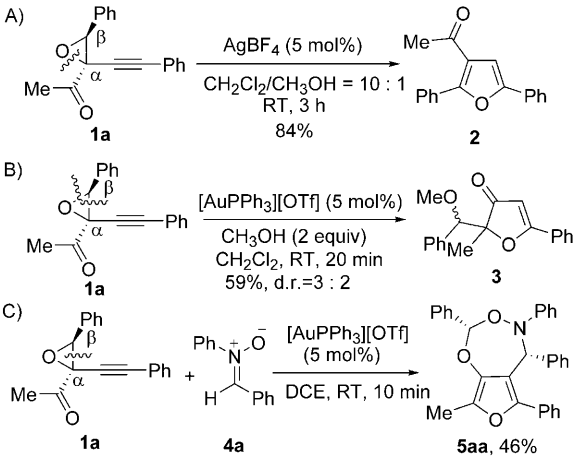
With this hypothesis in mind, we first developed a general and efficient route to β-alkyne-α,β-epoxy ketones **1**. Gratifyingly, these substrates can be easily prepared from α,β-unsaturated ketones. The successive bromination, elimination, and Sonagashira cross-coupling gives 2-(1-alkynyl)-2-alken-1-ones in high yields according to a known procedure.[10] A subsequent epoxidation reaction produces the desired products in moderate to high yields (Scheme 2). The structure of **1b** was established by spectroscopic analysis and further confirmed by single-crystal X-ray analysis.[11]



Scheme 2. The general route to β-alkyne-α,β-epoxy ketones **1**.

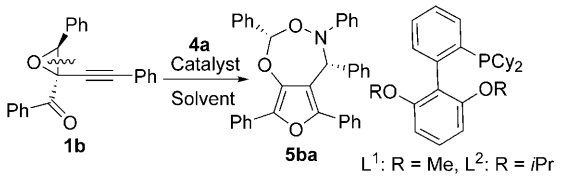
We initiated our investigation with the cycloisomerization of **1a**. When **1a** was subjected to $AgBF_4$ in a solvent mixture (CH_2Cl_2/MeOH = 10:1), cycloisomerization occurred and gave the trisubstituted furan **2** in 84% yield through C_α–O bond cleavage (Scheme 3A). Interestingly, upon reaction with 5 mol% [$AuPPh_3$][OTf] (OTf = triflate; Scheme 3B), compound **1a** afforded a highly substituted furan-3(2H)-one **3** in 59% yield and 3:2 diastereoisomeric ratio (d.r.). Both C–C and C_β–O bond cleavage are involved in this process.

We then studied the other more difficult C–C bond cleavage pathway. To our delight, this pathway was achieved when a mixture of **1a** and nitrone **4a** were subjected to [$AuPPh_3$]Cl and AgOTf in 1,2-dichloroethane (DCE) at RT to give the desired bicyclic compound **5aa** along with an unidentified product (Scheme 3C). Inspired by this result, we further optimized the reaction conditions by using ketone **1b** and nitrone **4a** as model substrates (Table 1). The effect



Scheme 3.

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



Entry	Catalyst	Solvent	Time	Yield[e] [%]
1	[$AuPPh_3$][OTf]	DCE	10 min	80 (75)
2	[$AuPPh_3$][SbF_6]	DCE	10 min	84 (79)
3	[$AuPPh_3$][BF_4]	DCE	10 min	83 (76)
4	[AuIPr][OTf]	DCE	4 h	38
5	$AuCl_3$	DCE	11 h	51
6	[$AuPPh_3$][SbF_6]	CH_2Cl_2	10 min	79 (74)
7	[$AuPPh_3$][SbF_6]	toluene	10 min	87 (75)
8	[$AuPPh_3$][SbF_6]	CH_3CN	10 min	42
9	[$AuPPh_3$][SbF_6]	THF	10 min	33
10[b]	[$AuPPh_3$][SbF_6]	DCE	10 min	81 (79)
11[c]	[$AuPPh_3$][SbF_6]	DCE	10 min	83 (77)
12[d]	[AuL^1][SbF_6]	DCE	1 h	98 (90)
13[d]	[AuL^2][SbF_6]	DCE	1 h	100 (93)

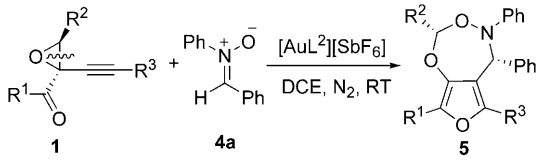
[a] Unless otherwise noted, reactions were performed with **1b** (0.3 mmol), **4a** (0.33 mmol), and catalyst (5.0 mol%) in DCE at RT. [b] 1.5 equiv of **4a**. [c] 2.0 equiv of **4a**. [d] Generated in situ from Me_2SAuCl, ligand, and $AgSbF_6$. [e] Yield obtained by NMR spectroscopy; the values given in parentheses indicate isolated yields.

of different counteranions were examined by the combination of [$AuPPh_3$]Cl with different silver salts, such as $AgSbF_6$ (Table 1, entry 2) and $AgBF_4$ (Table 1, entry 3). Of these two catalysts, [$AuPPh_3$][SbF_6] gave the highest isolated yield (79%, Table 1, entry 2). [AuIPr][OTf] (IPr = bis(2,6-diisopropylphenyl)imidazol-2-yliden) gave only 38% yield (Table 1, entry 4). The reaction took 11 h to go to completion when $AuCl_3$ was used, with only a 51% yield observed by NMR spectroscopy (Table 1, entry 5). Various solvents

and different amounts of nitrone were then investigated, but such changes did not improve the process (Table 1, entries 6–11). Considering ligand effects in gold-catalyzed reactions,[12,13] the 2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl (L^1, S-Phos) and 2-dicyclohexylphosphino-2′,6′-diisopropoxy-1,1′-biphenyl (L^2, Ruphos)-derived gold complexes were then examined (Table 1, entries 12 and 13); the latter gave the best result (93% yield).

A wide variety of 1-(1-alkynyl)oxiranyl ketones **1** were examined under the optimal conditions. The results are summarized in Table 2. The ketone substituent R^1 was either an

Table 2. Variation of 1-(1-alkynyl)oxiranyl ketones **1** component.[a]



1 **4a** **5**

Entry	$R^1/R^2/R^3$	Time [h]	Product (Yield[b] [%])
1	Ph/4-$MeOC_6H_4$/Ph (**1c**)	1.5	**5ca** (71)
2	Ph/4-$NO_2C_6H_4$/Ph (**1d**)	8	**5da** (81)
3	4-$MeOC_6H_4$/Ph/Ph (**1e**)	3	**5ea** (88)
4	4-ClC_6H_4/Ph/Ph (**1f**)	1	**5fa** (98)
5	Ph/Ph/*n*Bu (**1g**)	2	**5ga** (84)
6	Ph/Ph/cyclohexenyl (**1h**)	1	**5ha** (81)
7	Ph/Ph/4-$MeOC_6H_4$ (**1i**)	1	**5ia** (76)
8	Me/Ph/4-$MeOC_6H_4$ (**1j**)	3	**5ja** (69)
9	Me/4-ClC_6H_4/Ph (**1k**)	10.5	**5ka** (64)

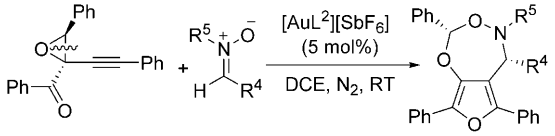
[a] Unless otherwise noted, reactions were performed with 0.3 mmol of **1**, 0.33 mmol of **4a**, 5.0 mol% of [AuL^2]Cl, and $AgSbF_6$ (1:1) in 3.0 mL of DCE at RT. [b] Isolated yield.

aromatic ring or an alkyl group. For those substrates with an aromatic R^1, the reactions normally gave the corresponding cycloadducts in good to excellent yields (Table 2, entries 1–7); for alkyl-substituted substrates, the reactions proceeded smoothly to afford the desired products in good yields (Table 2, entries 8 and 9). Both electron-withdrawing and -donating groups could be introduced to the phenyl ring (R^{1-3}). Note that *cis* adducts were only detected for **5**, indicating that this reaction is highly chemo-, regio-, and stereoselective. The structure of **5ja** was established by spectroscopic analysis and further confirmed by single-crystal X-ray analysis.[11]

The scope of this reaction was next examined by varying nitrone **4** (Table 3). *para*-Methoxy- or *para*-nitrobenzaldehyde-derived nitrones gave the corresponding products in high yields with excellent diastereoselectivity (>20:1) (Table 3, entries 1 and 2). Furyl and stryryl could also be incorporated as the R^4 group into the products (Table 3, entries 3 and 4). Halogens at the R^4 and R^5 positions makes further functionalizations possible (Table 3, entries 5, and 7–9).

A plausible mechanism that accounts for this gold(I)-catalyzed, highly diastereoselective [4+3] cyclization is depicted in Scheme 4. The gold(I) coordination of the triple bond of

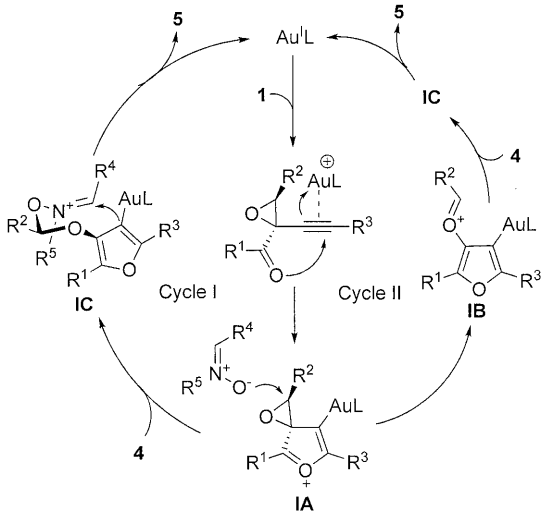
Table 3. Reactions of **1b** with various nitrones.[a]



1b **4** **5**

Entry	R^4/R^5	Time [h]	Product (Yield[b] [%])
1	4-$MeOC_6H_4$/Ph (**4b**)	5	**5bb** (89)
2	4-$NO_2C_6H_4$/Ph (**4c**)	10	**5bc** (82)
3	furyl/Ph (**4d**)	10	**5bd** (79)
4	styryl/Ph (**4e**)	10	**5be** (80)
5	4-BrC_6H_4/Ph (**4f**)	0.5	**5bf** (97)
6	Ph/4-MeC_6H_4 (**4g**)	0.5	**5bg** (89)
7	Ph/4-BrC_6H_4 (**4h**)	0.5	**5bh** (90)
8	Ph/3-ClC_6H_4 (**4i**)	1	**5bi** (86)
9	4-$OMeC_6H_4$/4-BrC_6H_4 (**4j**)	0.5	**5bj** (89)

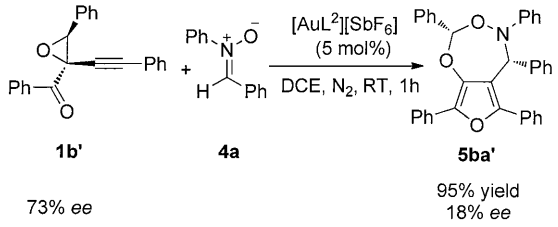
[a] Unless otherwise noted, reactions were performed with **1b** (0.3 mmol), **4** (0.33 mmol), [AuL^2]Cl (5 mol%), and $AgSbF_6$ (5 mol%) in DCE (3.0 mL) at RT. [b] Isolated yield.



Scheme 4. Plausible mechanism.

1 enhances the electrophilicity of the alkyne. Subsequent nucleophilic attack of the carbonyl oxygen on the gold(I)-activated alkyne forms the oxonium-containing vinyl–gold intermediate **IA**.[8f,14] Intermediate **IA** may undergo two different reaction pathways (cycle I and II). In cycle I, the regioselective homo-Michael addition of nitrone **4** at the C_β position of the epoxy motif would generate furanyl–gold intermediate **IC**, which in turn, upon ring closure through the favored chairlike conformation, would give the formal [4+3] cycloadduct in a highly diastereoselective fashion and regenerate the gold catalyst. Alternatively, intermediate **IA** could undergo aromatization through C–C bond cleavage of the epoxy motif to produce furanyl–gold intermediate **IB** with an oxygen-stabilized carbocation (cycle II), which would react with nitrone **4** to give the same intermediate **IC** as in cycle I.

To gain further insight into the mechanism, enantioenriched substrate **1b′** (with 73% enantiomeric excess (*ee*)) and **4a** were subjected to the standard reaction conditions. After 1 h, compound **5ba′** was obtained in 95% yield, with only 18% *ee*. This indicates that both pathways (cycles I and II) are involved in the process (Scheme 5).



Scheme 5. Reaction of enantioenriched substrate **1b′** with **4a**.

In conclusion, we have successfully developed a novel facile strategy towards chemoselective C–C bond cleavage[15] of epoxides by introducing a side chain (alkyne) that can be selectively activated by a catalyst. Furthermore, novel hetero-bicyclics **5** can be efficiently prepared in a highly diastereoselective fashion from readily available 1-(1-alkynyl)oxiranyl ketones and nitrones. The application of this novel activation strategy towards chemoselective C–C activation of epoxides to other oxiranyl derivatives is being carried out in our laboratory and will be reported in due course.

Experimental Section

General procedure for the synthesis of 5ba: $[AuL^2]Cl$ (10.5 mg, 0.015 mmol) and $AgSbF_6$ (5.2 mg, 0.015 mmol) were mixed and stirred for 10 min in anhydrous DCE (1 mL) under N_2. The mixture was transferred to **1b** (97.3 mg, 0.3 mmol) and **4a** (65.1 mg, 0.33 mmol) in anhydrous DCE (2 mL), the resulting reaction mixture was stirred at RT for 1 h under N_2. After evaporation under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1) to afford **5ba** as a white solid (145.6 mg, 93%). M.p. 171–173 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.97$ (d, $J = 7.8$ Hz, 2H), 7.68–7.65 (m, 2H), 7.50–7.29 (m, 11H), 7.24–7.18 (m, 7H), 6.99–6.92 (m, 3H), 6.47 (s, 1H), 5.99 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz): $\delta = 149.0$, 145.9, 143.2, 138.7, 136.5, 135.5, 130.7, 130.2, 130.0, 129.2, 128.73, 128.68, 128.58, 128.4, 127.9, 127.9, 127.8, 126.7, 126.6, 126.2, 124.0, 123.1, 118.5, 118.1, 108.8, 70.4 ppm; IR (neat): $\tilde{\nu} = 3061$, 3030, 1597, 1490, 1345, 1190, 989, 851, 762, 691 cm^{-1}; MS (EI, 70 ev): *m*/*z* (%): 521 (0.17) $[M]^+$, 77 (100); HRMS: *m*/*z* calcd for $C_{36}H_{27}NO_3$: 521.1991, found: 521.1993.

Acknowledgements

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Keywords: C–C bond cleavage · cycloaddition · epoxides · gold · nitrones

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[11] CCDC-784754 (**1b**) and 784755 (**5ja**) contain 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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