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Gold-Catalyzed Oxidation of Thioalkynes To Form Phenylthio Ketene Derivatives via a Noncarbene Route

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S Supporting Information

ABSTRACT: Gold-catalyzed oxidations of thioalkynes with 8-methylquinoline oxides afford 2-phenylthioketenes that can be trapped efficiently with alcohols. The synthetic utility is manifested by terminal and internal thioalkynes over a wide scope, bearing esters, ketones, alkyl, and oxime substituents. Our density functional theory calculations suggest that gold-catalyzed oxidations of terminal and internal thioalkynes with 8-methylquinoline oxides generate gold-bound ketene intermediates without the intermediacy of α -oxo gold carbene.

ArS--------R [Py]⁺-O⁻ + Nu-H `X. ArS R = H. alkyl, ester not formed LAU LAu

he Wolff rearrangement refers to the transformation of α diazocarbonyl species into ketene intermediates via a 1,2group migration of α -oxo carbenes I (X = alkyl, aryl, and heteroatom); the reactions were first reported by Wolff one century ago.¹ The synthetic utility of this rearrangement is commonly manifested by trapping these ketene species with nucleophiles (Nu-H) to give ketene addition products (eq 1). The high reliability of this rearrangement is typically achieved by thermolysis,^{2a,b} photolysis^{2c-e} or Ag(I)-catalyzed³ diazo decompositions (eq 1). In the presence of Au(I),^{4a-d} Cu(I),^{4e-g} Pd(II),^{5a} Rh(II),^{5b-f} and Fe(II)^{5g} catalysts, these α -diazocarbonyl precursors typically yield carbene insertion products (eq 2). Notably, Rh(II) catalysts can implement the Wolff rearrangement of α -diazo esters of special types.⁶



One recent advance in gold catalysis is the generation of α oxo gold carbenes (III) from the catalytic oxidations of alkynes with pyridine-based oxides;^{7a-c} the significance of this gold catalysis is to employ readily available alkynes as α -diazo carbonyl surrogates. These gold carbenes are generally trapped with nucleophiles (Nu-H) to yield carbene Nu-H insertion products exclusively (eq 3).^{7d-k} Alkynes are inexpensive and readily available, compared to α -diazo carbonyl reagents. We sought to use alkyne⁸ as ketene precursors via gold-catalyzed oxidations of alkynes. In contrast with ynamides, the utility of thioalkynes have been little explored in gold catalysis, although

the sulfur atom can enhance the electrophilicity of gold- π alkynes toward nucleophiles.⁹ We report the development of this new ketene synthesis on thioalkynes; astonishingly, this alkyne oxidation generates ketene intermediates without prior formation of α -oxo gold carbenes for both terminal and internal alkynes. A weak S…Au interaction in intermediate IV facilitates this 1,2-sulfur shift. A notable feature of this catalysis is the wide scope of thioalkynes bearing hydrogen, alkyl, esters, ketones, and oxime ethers. In contrast, the use of α -diazo thiol esters^{6c} for the Wolff rearrangement is severely limited to the unsubstituted type (R = H), as noted in eq 5. We selected thioalkynes as a target because α -diazo thiol ester (I) can generate a ketene species (II) efficiently with thermolysis or by Rh(II) catalysis,^{6c} as depicted in eq 5; however, these diazo species could not be prepared for an alkyl- or aryl-substituted form (R = alkyl or aryl).

Alkyne oxidation via gold carbenes





Initial tests of terminal thioalkyne 1a with LAuCl/AgNTf₂ $[L = P(t-Bu)_2(o-biphenyl)]$ with 8-methylquinoline oxide 2a in

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1:2.5 and 1:1.2 proportions in DCE/MeOH (10/1, 25 °C) yielded methyl 2-(phenylthio)acetate **3a** in 65% and 84% yields, respectively (see Table 1, entries 1 and 2). Other

Table 1. Oxidative Rearrangement of Thioalkyne 1a with Gold Catalysts



				Yield ^b (%)	
entry	catalyst	x	time (h)	3a	1a
1	LAuCl/AgNTf ₂	2.5	8	65	-
2	LAuCl/AgNTf ₂	1.2	8	84	_
3	IPrAuCl/AgNTf ₂	1.2	20	32	55
4	(PhO) ₃ PAuCl/AgNTf ₂	1.2	13	65	-
5	PPh ₃ AuCl/AgNTf ₂	1.2	8	84	_
6	LAuCl/AgOTf	1.2	8	85	_
7	LAuCl/AgSbF ₆	1.2	8	84	_
8	AgNTf ₂	1.2	24	14	66
9	HOTf	1.2	24	_	22

^{*a*}[1a] = 0.18 M. ^{*b*}Product yields are reported after purification from a silica column, $L = P(t-Bu)_2(o-biphenyl)$, IPr = 1,3-bis-(diisopropylphenyl)-imidazol-2-ylidene.

catalysts including L'AuCl/AgNTf₂ (L' = IPr, P(OPh)₃, PPh₃) gave compound **3a** in yields of 32%–84% with PPh₃AuCl being the most efficient (Table 1, entries 3–5). A variation of the silver salts¹⁰ such as LAuCl/AgX (X = OTf and SbF₆) maintained the high efficiency, affording compound **3a** in yields of 84%–85% (Table 1, entries 6 and 7). In contrast, AgNTf₂ was an inefficient catalyst to deliver compound **3a** in only 14% yield over a 24 h period (Table 1, entry 8). The spectral data of compound **3a** are identical to those reported in the literature.¹¹

We assessed the scope of this oxidative rearrangement using various terminal thioalkynes and alcohols ROH (R = alkyl and phenyl; see Table 2). In the oxidations of thioalkyne 1a with 8-

Table 2. Oxidative Rearrangement with Various Terminal Thioalkynes



"[1] = 0.18 M. ^bProduct yields are reported after purification from a silica gel column.

methylquinoline oxide 2a with various ROH (R = Et, *i*-Pr, Ph and CH₂Ph), rearrangement products 3b-3e were obtained in yields of 79%–90% (Table 2, entries 1–4). For various 4-phenyl-substituted thioalkynes 1b–1e (X = Me, OMe, F, and Cl), their oxidative rearrangement with methanol yielded the desired products 3f–3i in yields of 83%–94% (Table 2, entries 5–8). The scope of these new catalytic oxidations is significantly expanded with its applicability to thioalkynyl esters 4 (Table 3). This new substrate scope is synthetically significant because α -diazo thiol esters can only be prepared in unsubstituted form (eq 5). Entries 1–5 in Table 3 show the

 Table 3. Oxidative Rearrangement with Various Thioalkynyl Esters



^{*a*}[4] = 0.13 M. ^{*b*}Product yields are reported after isolation from a silica column.

alternations of 4-phenyl substituents of thioalkynes 4a-4e (X = H, Me, OMe, Cl, and F) to afford the desired 2phenylthiomalonates 5a-5e in 82–88% yields (Table 3, entries 1–5). For 3-methoxyphenyl, 1- or 2-naphthyl thioalkynes (4f-4h), their resulting compounds (5f-5h) were produced in satisfactory yields (84%–88%; see Table 3, entries 6–8). This rearrangement is compatible with various alcohols Nu-H = *i*-PrOH and BnOH, yielding the rearrangement products 5i and 5j in yields of 85%–88% (Table 3, entries 9 and 10).

This oxidative rearrangement is compatible also with thioalkynyl ketones 6 to form 2-phenylthio α -ketoesters 7/7' in a keto/enol mixture efficiently; herein, enol forms 7 are the dominant species (seeTable 4). Entries 1–3 in Table 4 show

Table 4. Oxidative Rearrangement with Various ThioalkynylKetones



 $a^{[6]} = 0.14$ M. ^bProduct yields are reported after isolation from a silica gel column.

the variations of ketones (R = Me, *i*-Pr, and *n*-butyl) of thioalkynes **6a**-**6c**, affording the desired products 7a'-7c'7c' in yields of 71%-83% (Table 4, entries 1-3). Thioalkynes bearing various 4-phenylthio moieties **6d**-**6g** (X = Cl, F, Me, and OMe) were also compatible with this new rearrangement to deliver products 7d/7d'-7g/7g' in 87%-92% yields (Table 4, entries 4-7). For 3-methoxyphenyl thioalkyne (6h), its gold-catalyzed reaction led to the desired product 7h/7h' in 91% yield (Table 4, entry 8). We also tested the reactions on 1- and 2-naphthyl thioalkyne analogues **6i**-**6j**, further yielding β -keto esters 7i/7i' and 7j/7j' in yields of 92%-94% (Table 4, entries 9 and 10, respectively). We also achieved new oxidative rearrangement of thioalkynyl oxime ethers **8** to yield 2-(phenylthio)-2H-azirine-2-carboxylates **9**, of which the pro-

Table 5. Catalytic Oxidative Cyclization via Wolff Rearrangement



 $a^{a}[\mathbf{8}] = 0.10$ M. ^bProduct yields are reported after isolation from a silica gel column.

In entry 3 in Table 5, we obtained byproduct 9''c, arising from a decarboxylation of β -oxime acid 9'. Entries 1-4 in Table 5 show the compatibility of this new arrangement with alkynyl oxime ethers 8a-8d bearing various 4-phenylthio moieties, yielding 2H-azirine derivatives 9a-9d in yields of 62%-68% (Table 5, entries 1-4); compound 9d was also characterized by 2D HMBC NMR spectra, indicating a linkage of *n*-butyl to the iminoyl carbon. This oxidative rearrangement is operable also with 1- and 2-naphthylthio derivatives 8e and 8f, further yielding 2H-azirine products 9e and 9f in yields of 69%-71% (Table 5, entries 5 and 6). For 3-methoxyphenylthio alkyne 8g, its resulting 2H-azirine 9g was obtained in 67% yield (Table 5, entry 7). We varied the oxime ethers with R =Ph and *i*-Pr as in species 8h and 8i that afforded the desired 2H-azirine derivatives 9h and 9i in yields of 61%-65% (Table 5, entries 8 and 9).

To our pleasure, this oxidative rearrangement was applicable even to alkyl-substituted thioalkynes 10a-10c (R = *n*-butyl, cyclopropyl, and isopropyl), yielding the Wolff rearrangement product 11a-11c in a major proportion (58%-65%), whereas an unsaturated thioester (11a') was isolated in only 10% yield for R = *n*-butyl (see eqs 6 and 7). Notably, our DFT calculations suggest that compounds 11a and 11a' are produced from the same gold enol ether intermediates Int-3' other than α -oxo gold carbenes (see Figure 2, vide infra). Treatment of α -diazo thiol ester 12a with a gold catalyst gave a Wolff rearrangement product 3a very efficiently (eq 8). We failed to prepare *n*-butyl-derived α -diazo thiol ester 12b, which remains unknown in the literature^{6c} (eq 8).



Density functional theory (DFT) calculations were performed to provide more insights into the reaction

mechanism. For terminal thioalkyne 1a, the formation of gold-containing enol ether Int-3 from gold π -thioalkyne (Int-2) has $\Delta G^{\ddagger} = 16.9$ kcal/mol and $\Delta G = 7.5$ kcal/mol (Figure 1). Notably, we are unable to find a feasible route to yield α -



Figure 1. Gibbs free-energy surface for the conversion of the gold π -thioalkyne intermediate to gold-bound ketenes. The structure of **TS-34** is shown below the energy profile along with the Newman project for the C=C bond. Values are given in units of kcal/mol.

oxo gold carbenes (**Int-1**); removing 8-methyl quinoline leads directly to the formation of gold-bound ketenes **Int-4** with $\Delta G^{\ddagger} = 4.8$ kcal/mol and $\Delta G = -66.7$ kcal/mol. This is probably due to the strong affinity of PhS toward 1,2migration, as evidenced by the very negative reaction free energy. Note that, in **TS-34**, the four atoms bound to C==C are not coplanar; therefore, the lone pair of S is able to interact with the unoccupied C==C π^* -orbital, causing the migration of -S-Ph to form the ketene intermediate. In the case of *n*-butylsubstituted thioalkyne, the formation of gold-containing enol ether **Int-3'** from **Int-2'** has $\Delta G^{\ddagger} = 22.8$ kcal/mol and $\Delta G =$ 14.7 kcal/mol (Figure 2). Dissociation of 8-methyl quinoline



Figure 2. Gibbs free-energy surface for the conversion of the goldbounded π -thioalkyne *n*-butyl substituted to the corresponding goldbound ketene intermediate. Values are given in units of kcal/mol.

results in the formation of gold-bound ketene (Int-4') with $\Delta G^{\ddagger} = 3.1$ kcal/mol and $\Delta G = -72.4$ kcal/mol. Thus, as compared to the terminal thioalkyne case, we find that the replacement of H by *n*-butyl makes C–O coupling less favorable but 8-methyl quinoline dissociation more favorable. Interestingly, besides the ketene formation pathway, we find an additional route, in which 8-methyl quinoline dissociation from Int-3' is accompanied by *n*-butyl α - proton migration to a base.

с

When another 8-methyl quinoline is used as the base, ΔG^{\ddagger} and ΔG were calculated to be 18.7 and -83.2 kcal/mol (Int-3' \rightarrow TS-35' \rightarrow Int-5'), respectively.

The higher ΔG^{\ddagger} value than that for Int-3' \rightarrow TS-34' \rightarrow Int-4', which is due to the entropic cost involved in bringing two molecules together, suggests that this pathway only plays a minor role.

We postulate a mechanism¹² depicted in Scheme 1 to rationalize the Wolff rearrangement products. A notable

Scheme 1. Plausible Mechanism



feature is the formation of gold enolates such as In-6 after a Nu-H addition. For gold-bound ketenes bearing oxime ethers In-4', their initially formed C-bound enolates In-7 equilibrate with their O-bound enolates In-8, before an intramolecular cyclization to yield the observed products 9. In this process, transformations of species In-7 and In-8 into highly strained azacycles 9 involve a release of gold moiety, resulting in an increase in entropy.

In summary, this work reports gold-catalyzed oxidative rearrangement of thioalkynes¹³ using 8-methylquinoline oxides and alcohols, yielding the Wolff rearrangement products. In contrast with α -diazo thiol esters, which are restricted to the unsubstituted type. The substrate scope of thioalkynes is wide, including terminal and internal alkynes bearing esters, ketones, and even alkyl substituents, further broadening the synthetic utility. Interestingly, thioalkynyl oxime ethers were also applicable substrates to yield 2*H*-azirine-2-carboxylate derivatives. Our DFT calculations indicate that gold-catalyzed oxidations¹⁴ of terminal and internal thioalkynes with *N*-oxides generate gold-bound ketene intermediates, favorably from both kinetic and thermodynamic aspects. Herein, α -oxo gold carbenes are not the precursors to gold-bound ketenes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b01768.

Experimental procedures, characterization data, crystallography data, and ¹H NMR and ¹³C NMR for representative compounds (PDF)

Accession Codes

CCDC 1888301 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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$$\begin{bmatrix} \stackrel{+}{\mathsf{AuL}} \\ \mathsf{S}\stackrel{-}{\stackrel{-}{=}} \\ \mathsf{Ph} \end{bmatrix} \xrightarrow{\mathsf{S}^{\mathsf{t}}} \underset{\mathsf{Ph}}{\overset{\mathsf{AuL}}}$$

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$$\overbrace{\begin{matrix} \bigcirc \bar{\mathsf{O}}^- Z^+ \\ R' \xrightarrow[]{=} \\ [Au] \end{matrix}}^{\bigcirc \mathsf{O}^- Z^+} \underset{\mathsf{R}'}{\overset{\mathsf{O}}{\longrightarrow}} \underset{\mathsf{A}u}{\overset{\mathsf{O}}{\longrightarrow}} \underset{\mathsf{R}' \xrightarrow{\mathsf{O}}{\longrightarrow}}^{\bigcirc \mathsf{O}} \underset{\mathsf{SiR}_3}{\overset{\mathsf{O}}{\longrightarrow}} \underset{\mathsf{SiR}_3}{\overset{\mathsf{O}}{\longrightarrow}} \underset{\mathsf{SiR}_4}{\overset{\mathsf{O}}{\longrightarrow}} \underset{\mathsf{O}}{\overset{\mathsf{O}}{\longrightarrow}} \underset{\mathsf{O}}{\overset{\mathsf{O}}{\rightthreetimes}} \underset{\mathsf{O}}{\overset{\mathsf{O}}{\to}} \underset{\mathsf$$

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