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Gold-catalyzed formal $[4\pi + 2\pi]$ -cycloadditions of propiolate derivatives with unactivated nitriles[†]

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Gold-catalyzed hetero- $[4\pi + 2\pi]$ -cycloadditions of *tert*-butyl propiolates with unactivated nitriles are described; the resulting 6*H*-1,3-oxazin-6-ones are not easily accessible *via* conventional methods. This new finding enables a one-pot gold-catalyzed synthesis of highly substituted pyridines through sequential gold-catalyzed reactions of *tert*-butyl propiolates with nitriles, and then with electron-deficient alkynes in the same solvent. The utility of these [4 + 2]-cycloadditions is further expanded with various aldehydes, ketones and 2-phenyloxetane, yielding satisfactory yields of cycloadducts.

Introduction

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Metal-catalyzed $[4\pi + 2\pi]$ -cycloadditions are powerful tools for the construction of carbo- or heterocyclic frameworks.^{1,2} Although common nitriles and alkynes represent common triple bond motifs, nitriles are generally less reactive than alkynes in catalytic $[4\pi + 2\pi]$ -cycloadditions; the chemical stability of nitriles is reflected by their bond energy (854 kJ mol^{-1}), being larger than that of alkynes (835 kJ mol^{-1}).³ For instance, thermal $[4\pi + 2\pi]$ -cycloadditions of dienes with unactivated nitriles required 600 °C (2 min) to give pyridine derivatives in 0.1–0.5% yields.^{4a} In the context of catalytic $[4\pi +$ 2π -cycloadditions, not surprisingly, only one literature report documents both nitrile/1,3-diene and nitrile/1,3-enyne systems (eqn (1) and (2)).^{4b,c} Ogoshi reported the first formal [4 + 2]cycloadditions of common nitriles with dienes using Ni(0) catalysts (eqn (1)).^{4b} Although Barluenga and Aguilar reported formal $[4\pi + 2\pi]$ -cycloadditions of some 3-en-1-ynes with unactivated nitriles,4c such highly functionalized 3-en-1-ynes (X = *cis*-unsaturated ester, Z = alkoxy) are too specialized to reflect the reaction generality (eqn (2)). The $[4\pi + 2\pi]$ -nitrile cycloadditions still remain an unsolved task for O- and N-substituted analogues of 1,3-dienes and 1,3-enynes (X = O, NR', eqn(1) and (2)).⁵ In a significant advance, we here report the gold-catalyzed formal hetero- $[4\pi + 2\pi]$ -cycloadditions^{6,7} of various propiolates with nitriles to afford 6H-1,3-oxazin-6-ones efficiently (eqn (3)).8 These findings enable the development of new cascade cycloadditions using three π -motifs including propiolates, nitriles and alkynes, yielding highly substituted pyridine derivatives. Notably, 6H-1,3-oxazin-6-ones are useful intermediates in various organic reactions whereas highly substituted pyridines

are important structural cores commonly found in many bioactive molecules (see ESI Fig. S1 \dagger);^{9,10} their availability from convenient *t*-butyl propiolates increases the synthetic utility of this gold catalysis.

$$X \xrightarrow[R]{} N \xrightarrow{\text{unknown}} X = 0, \text{ NR}' \xrightarrow[R]{} X \xrightarrow[R]{} \frac{\text{Ni}(0)}{\text{X} = \text{CH}_2} \xrightarrow[R]{} N \xrightarrow[R]{} (1)$$

$$\underbrace{\overset{\text{4+2-}}{\overset{\text{cycloadducts}}}}_{X = O, NR'} \underbrace{\overset{\text{Y}}{\underset{X = +}{\overset{\text{+}}{\overset{\text{+}}{\underset{R = C \equiv N}{\overset{\text{+}}{\underset{R = cis-CH = CHCO_2Me}{Z = OMe}}}}_{R'' = cis-CH = CHCO_2Me} (2)$$

This work
two-component cycloadditions

$$R^1 = CO_2(t-Bu)$$

 $R^1 = H$, alkyl and aryl
 $R^2-C\equiv N$
 $R^2-C\equiv N$
 R^2
 R^2

cascade cycloaddition series

$$R^{1} \longrightarrow CO_{2}(t-Bu) \xrightarrow{(1) [Au]/R^{2}-C \equiv N}_{(2)R^{3} \longrightarrow -EWG} \xrightarrow{R^{1}}_{N} \xrightarrow{R^{3}}_{EWG}$$
(4)

Results and discussion

We envisage that direct $[4\pi + 2\pi]$ -cycloadditions of propiolate derivatives with nitriles provide the most convenient synthesis of 6*H*-1,3-oxazin-6-ones such as **3**; the current procedures rely mainly on thermal rearrangement of *N*-acyl β -



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lactams.^{8a-d} To test the feasibility, as shown in Table 1, tertbutyl hept-2-ynoate (1a, 1 equiv.) was treated with benzonitrile 2a (3 equiv.) and AuCl₃ (5 mol%) in hot DCE (70 °C, 16 h), affording the desired product 3a in only a small yield (5%) together with the initial 1a in 45% recovery (entry 1). The use of PPh₃AuCl/AgSbF₆ significantly increased the yield of the desired 3a to 51% (entry 2). We also examined other cationic gold catalysts (5 mol%) including IPrAuCl/AgSbF₆ and P(t-Bu)₂(o-biphenyl)AuCl/AgSbF₆, yielding compound 3a in 64% and 85% yields, respectively (see entries 3 and 4). With the alteration of the silver salts as in $P(t-Bu)_2$ -(o-biphenyl)AuCl/AgX ($X = NTf_2$ and OTf), the product yields slightly decreased to 77% and 72%, respectively (entries 5 and 6). AgSbF₆ (70 °C, 24 h) and $Zn(OTf)_2$ (19 h) were found to be inactive in DCE, leading to a recovery of the starting compound 1a in 72-75% yield (entries 7 and 8). The use of In(OTf)₃, Sc(OTf)₃ and TfOH in DCE gave hept-2-ynoic acid 1a' in 65-72% yield and amide species 2a-H (25-35% yield) along with unreacted starting compound 1a (5-15% yield, entries 9-11). The yields of compound 3a varied with the solvents (70 °C), with 65% in toluene (22 h), 82% in C₆H₅Cl (18 h) and 56% in 1,4-dioxane (19 h, entries 12-14).

Table 2 assesses the reaction generality using various propiolate derivatives with varied nitriles. We first examined the reactions with unsubstituted propiolate species **1b**; its cycloaddition with benzonitrile **2a** proceeded smoothly to form the formal cycloadduct **3b** in 65% yield (entry **1**). The reaction scope is extensible to aliphatically substituted

propiolate species 1c-1e (R = isopropyl, cyclopropyl and cyclohexyl), yielding the desired products 3c-3e in satisfactory yields (77-85%, entries 2-4). This formal cycloaddition is also applicable to alkenyl-substituted propiolate 1f to afford the corresponding product 3f in 68% yield (entry 5). We tested the reactions on various phenyl-substituted propiolate species **1g–1j** bearing various *para*-substituents (X = H, OMe, F andCl); their resulting cycloadducts 3g-3j were obtained in satisfactory yields (65-72%, entries 6-9). We performed an Xray diffraction study of product 3g to confirm its molecular structure.11 We also prepared 2- and 3-thienyl-substituted propiolate derivatives 1k and 1l; their reactions with benzonitrile afforded cycloadducts 3k and 3l in reasonable yields (entries 10 and 11, 55-58%). Entries 12-15 show the tests of tert-butyl hept-2-ynoate 1a with benzonitriles 2b-2e bearing various para-substituents (X = OMe, Me, CO_2Me , Cl) that afforded the desired cycloadducts 3m-3p in satisfactory yields (62–76%). These catalytic cycloadditions were compatible with disparate nitriles including cyclohexyl nitrile (2f), cinnamonitrile (2g) and 3-thienyl nitrile (2h), affording the expected products 3q-3s in satisfactory yields (66-78%, entries 16-18).

As inferred from the chemistry of 2*H*-pyran-2-ones,^{12,13} one representative compound **3a** (1 equiv.) was treated with diethyl but-2-ynedioate (4 equiv.) in hot *p*-xylene (150 °C, 10 h) to afford tetrasubstituted pyridine **5a** in 96% yield; this reaction sequence presumably proceeds with intermediate I that is prone to a loss of CO_2 (eqn (5)). As chlorobenzene is also an effective solvent for such a nitrile/ propiolate cycloaddition (Table 1, entry 9), we developed a



Table 1 Tests of propiolate derivatives with gold catalysts

	•							
1	AuCl ₃	DCE	16	45	5	_	_	
2	Ph ₃ PAuCl/AgSbF ₆	DCE	12		51	_	_	
3	IPrAuCl/AgSbF ₆	DCE	19	—	64	—	—	
4	LAuCl/AgSbF ₆	DCE	18	_	85	_	_	
5	LAuCl/AgNTf ₂	DCE	20	_	77	_	_	
6	LAuCl/AgOTf	DCE	22		72	—	—	
7	$AgSbF_6$	DCE	24	75	_			
8	$Zn(OTf)_2^c$	DCE	19	72	—	—	—	
9	$In(OTf)_3^c$	DCE	18	15	—	72	35	
10	$Sc(OTf)_3^c$	DCE	22	10	—	65	32	
11	HOTf ^c	DCE	15	5	—	67	25	
12	LAuCl/AgSbF ₆	Toluene	22		65	—	_	
13	LAuCl/AgSbF ₆	C ₆ H ₅ Cl	18	—	82	—	—	
14	LAuCl/AgSbF ₆	1,4-Dioxane	19	—	56	—	_	

 a [1a] = 0.18 M. b Product yields are reported after purification using a silica column. IPr = 1,3-bis(diisopropyl phenyl)-imidazol-2-ylidene, L = P(*t*-Bu)₂(*o*-biphenyl), Tf = trifluoromethansesulfonyl. c Reactions carried out at room temperature.



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

one-pot reaction involving the prior heating of a chlorobenzene solution of propiolate derivative **1a**, benzonitrile (3 equiv.) and $P(t-Bu)_2(o-biphenyl)$ AuCl/AgSbF₆ (5 mol%) at 70 °C (18 h) in a sealed tube to ensure a complete consumption of starting compound **1a**; to this solution was added diethyl but-2-ynedioate (4 equiv.) with further heating at 150 °C for 20 h. This one-pot process delivered the desired pyridine **5a** in 80% yield (eqn (6)). If the three reactants in the same proportions were heated together with a gold catalyst in hot chlorobenzene (150 °C, 20 h), the yield of **5a** was decreased to 38% yield.



The easy operation of this one-pot reaction inspires us to examine the scope of the reaction using various propiolates, nitriles and alkynes; the results are summarized in Table 3. The procedures follow exactly that described in eqn (6). In the second stage of heating, the temperature is 150 °C for entries 1-7 and 180 °C for entries 8-12. Entry 1 shows the compatibility of these cycloadditions with unsubstituted propiolate derivative **1b** (R = H) that reacted sequentially with benzonitrile (2a) and diethyl but-2-ynedioate (4a) to yield the desired pyridine 5b in 45% yield. We also tested the reactions on various alkyl-substituted propiolates 1c-1e (R = isopropyl, cyclopropyl and cyclohexyl) that reacted with the same alkyne and benzonitrile to afford the desired pyridine species 5c-5e in 73–76% yields (entries 2–4). The reaction is further applicable to anyl-substituted propiolates 1g and 1l (R = Ph, 3-thienyl) to deliver the desired pyridines 5f and 5g in 61% and 51% yield, respectively (entries 5 and 6). We tested the reactions of model propiolate (1a) and diethyl but-2-ynedioate (4a) with various nitriles (R^1 = cyclohexyl, 3-thienyl and *trans*-styryl), affording the expected pyridine products 5h-5j in satisfactory yields (68-75%, entries 7-9). The reactions were extensible to various unsymmetric alkynes 4b-4f that reacted with propiolate (1a) and benzonitrile (2a) with excellent or high regioselectivity (entries 11-15). The reactions worked well for terminal alkynes 4b (EWG = COOMe) and 4c (EWG = COPh) to afford the desired pyridines 5k and 5l as single regioisomers, with respective yields of 83% and 76% (entries 10 and 11). For nbutyl propiolate 4d, this one-pot sequence gave two inseparable isomeric products 5m/5m' = 4/1, in a combined 82% yield (entry 12). For the other n-butyl and phenyl-substituted

ynones **4e** and **4f** (EWG = COPh), their reactions afforded **5n** and **5o** with excellent regioselectivity and satisfactory yields (81–84%) (entries 13–14). The structures of representative compounds **5m** and **5n** were confirmed by proton NOE effects whereas the structure of cycloadduct **5o** was elucidated with an HMBC experiment (see ESI†).

As nitriles are weakly nucleophilic, we envisage that aldehydes and ketones might be applicable substrates. To our pleasure, gold-catalyzed reactions of 3-phenylpropiolate 1g with benzaldehyde, phenyl methyl ketone and acetone in hot dichloroethane (DCE) proceeded smoothly to afford formal cycloadducts 6a-6c in high yields (86-89%, eqn (7)). The structure of compound 6a was determined by X-ray diffraction.11 These carbonyl cycloadditions were also applicable to alkylsubstituted propiolates (1a) and (1e), yielding the desired compounds 6d and 6e in 87% and 77% yield, respectively (eqn (8)). Such a reaction was, notably, accessible to an eightmembered oxacyclic compound 6f with 2.5 mol% 1,3-bis(diisopropyl phenyl)-imidazol-2-ylidene AuSbF₆; it was isolated as a single regioisomer with 67% yield with 2-phenyloxetane (3 equiv.) and its molecular structure has been confirmed by X-ray diffraction.11 The compatibility of this gold catalysis with aldehydes, ketones and oxetanes truly reflects a broad applicability of these cycloadditions.

Table 3 One-pot operations with nitriles, propiolates and alkynes



^{*a*} 5 mol% gold catalyst, $L = P(t-Bu)_2(o-biphenyl)$, R^1CN (3 equiv.), $R^2CC-EWG$ (4 equiv.), 150 °C for entries 1–9 and 180 °C for entries 10–14. ^{*b*} These data correspond to the reaction time t_1/t_2 .



Scheme 1 A postulated reaction mechanism.



[Au]' = 1,3-bis(diisopropyl phenyl)-imidazol-2-ylidene AuCl/AgSbF₆

Prior to this work, Shin reported gold-catalyzed [4 + 2]cycloadditions of alkenes with propiolic acid, which was, however, the only applicable substrate.^{6a} Here, we employ diverse propiolate substrates to comply with not only nitriles but also aldehydes, ketones and oxetanes. To understand this discrepancy, we performed the reaction of 3-phenylpropiolic acid (1g') with benzonitrile with the same gold catalyst in DCE, but the yield of the desired compound 1g was only 8%, much smaller than that (68%) of its tert-butoxy derivative 1g (Table 2, entry 5). Clearly, prior transformations of t-butoxy propiolates to the propiolate acids do not occur in the course of the reactions. For ethyl propiolate 1g'', its corresponding reaction with benzonitrile gave the amide-addition product 3g' in 68% yield (eqn (10)); under this condition, benzonitrile was not effectively transformed into benzamide with this gold catalyst.14



The control experiments in eqn (10) indicate a mechanism involving a prior formation of nitrilium species **B** via a π -alkyne activation, proceeding with an attack of nitrile at the gold- π alkyne species A. As shown in Scheme 1, we postulate that the tert-butyoxy group of species B increases the nucleophilicity of a carbonyl group to attack this nitrilium moiety efficiently. This process releases a tert-butyl cation to induce a demetalation to form the observed cycloadduct 3g. Beside nitriles, various aldehydes, ketones and oxetanes are more reactive than alkenes upon comparison of their applicable propiolates. We postulate that these nucleophiles generate intermediates B, E and F bearing a large positive charge on the reacting C_{α} -carbons because of their adjacent oxonium and ammonium centers. We envisage that the propiolate cycloadditions match well with those nucleophiles that can develop highly polarized carbocations through π -alkyne activations.

Conclusions

Unactivated nitriles are known to be stable triple-bond species, and their [4 + 2]-cycloadditions with 4π -bond motifs and other small molecules have few successful examples.15 This work reports the hetero- $[4\pi + 2\pi]$ -cycloadditions of *tert*-butyl propiolates and nitriles catalyzed by gold catalysts. Such formal cycloadditions are applicable to diverse tert-butyl propiolates and nitriles, yielding useful 6H-1,3-oxazin-6-ones, which are not readily prepared with current methods.8 This new finding enables a one-pot gold-catalyzed synthesis of highly substituted pyridines through sequential reactions of tert-butyl propiolates with nitriles, and then with electron-deficient alkynes in the same solvent. The utility of these [4 + 2]-cycloadditions is further expanded with various aldehydes, ketones and 2-phenyloxetane, vielding satisfactory vields of cycloadducts. This work provides a new version of tert-butyl propiolates that feature useful four-atom building blocks with polar π -bond motifs such as nitriles, aldehydes and ketones, although their reactions with alkenes were reported to be restrictive.8

Acknowledgements

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