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Gold-catalyzed [4+3]-Annulations of Benzopyriliums with Vinyldiazo Carbonyls to Form Bicyclic Heptatriene Rings with Skeletal Rearrangement

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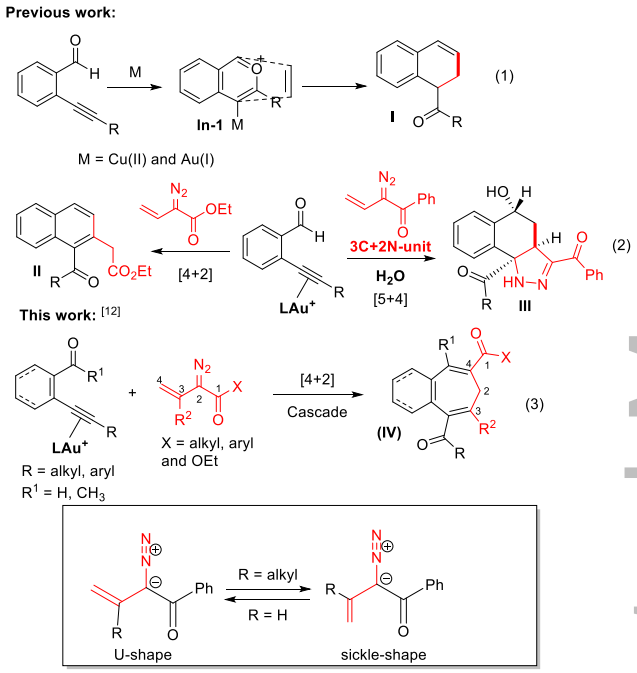
Abstract. We report gold catalyzed [4+3]-annulations between benzopyriliums and 3-alkyl-2-diazo-3-vinyl carbonyls, yielding 7*H*-benzo[7]annulene products efficiently. Notably, the carbon skeletons of resulting 7*H*-benzo[7]annulenes are structurally rearranged, accompanied by migrations of their alkyl and ketone motifs. Apart from applicable substrates over a wide scope, these annulatios are applicable to pyriliums and 3-alkyl-2-diazo-3-vinyl esters to increase their reaction significance. We postulate a mechanism involving an initial [4+2]-cycloaddition between benzopyriliums and 3-alkyl-2-diazo-3-vinyl carbonyl species, followed by formation of gold carbenes to induce a ring expansion and group migrations.

Keywords: Annulations; 2-Alkynylbenzaldehyde; Benzopyriliums; Rearrangement; Vinyldiazo carbonyls



Scheme 1. Reaction modes for benzopyriliums.

Stable vinyldiazo species[1-2] are versatile to undergo various cycloadditions with π-bond motifs, forming carbo- or heterocyclic rings of various sizes. Vinyldiazo carbonyl species are considered as electron-rich alkenes to serve as effective nucleophiles. Such species provide 2- or 3-carbon building units to undergo cycloadditions with electrophilic π-bond motifs, thus furnishing products with five- or six-membered rings.[3] Alternatively, these diazo species can be transformed into electrophilic vinylmetal carbenes that work as 1- or 3-carbon building units.[4] Benzopyrilium species **In-1** are versatile electrophilic 1,4-carbon dipoles[5] that undergo [4+2]-cycloadditions with alkynes,[6] alkenes,[7] furans,[8] aldehydes,[9] benzofurans[10] and isoxazoles,[11] leading exclusively to the formation of six-membered rings. Eq 1 shows a typical path for metal-catalyzed reactions of benzopyriliums **In-1** with alkenes.[7] We reported[12] gold-catalyzed reactions of vinyldiazo esters with benzopyriliums to yield [4+2]-cycloadducts **II**, following a typical path (eq 2). Notably, the use of vinyldiazo ketones in these reactions surprisingly afforded bicyclic azacyclic products[12] **III;** vinyldiazo ketones here become 5-atom building units (3C+2N) in these bicyclic annulations. We postulate[12] that the conformation of vinyldiazo ketones retains a U-shape to enable an initial [5+4]-cycloaddition, followed by an intramolecular cyclization (eq 2). In that work we mentioned[12] one specific example of [4+3]-annulations between benzopyriliums and 2-diazo-3-methyl-1-phenylbut-3-en-1-one (R^2 = Me) to yield one annulation product (**IV**) with skeletal rearrangement (eq 3). We proposed the change of chemoselectivity arose from an increased concentration of sickle-shaped conformation for this diazo species as the U-shape suffers steric interaction between alkyl and carbonyl groups. To verify this hypothesis and to test reaction generality, this work reports distinct [4+3]-annulations between

10.1002/adsc.202000292

benzopyriliums and 3-alkyl-2-diazo-3-vinyl ketones, which are accompanied by alkyl and ketone migrations. Apart from 3-alkyl-2-diazo-3-vinyl ketones and benzopyriliums, these new annulations are extensible to pyriliums and 3-alkyl-2-diazo-3-vinyl esters, reflecting applicable substrates over a wide scope.

The significance of this reaction is to provide an easy access to 6,7,8,9-tetrahydro-5*H*-benzo[7]annulene frameworks (**V**) that are commonly found as the structural cores of bioactive molecules **V-1** to **V-7** (Figure 1). Compounds **V-1** and **V-2** have been demonstrated to be potent inhibitors of tubulin polymerization and of growth of human cancer cell lines, thus showing anti-mitotic activity.[13a] Compounds **V-3** and **V-4** are natural products isolated from hairy root cultures of Salvia broussonetii.[13b-c] Compound **V-5** is biogenetically produced on oxidation of pyrogallol; its analogues compound **V-6** is natural pigments.[13d] Compounds **V-7** are potent and specific α_v integrin antagonists.[13d-e]

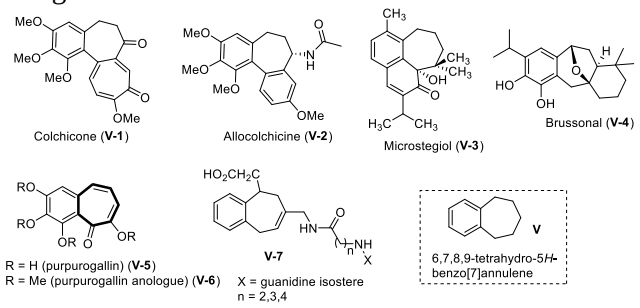
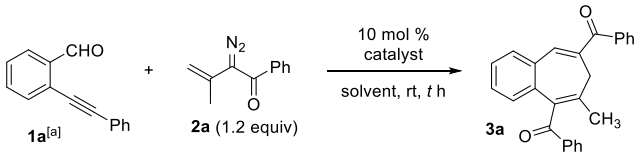


Figure 1. Representative bioactive molecules.

Table 1. Optimization of the reaction conditions.



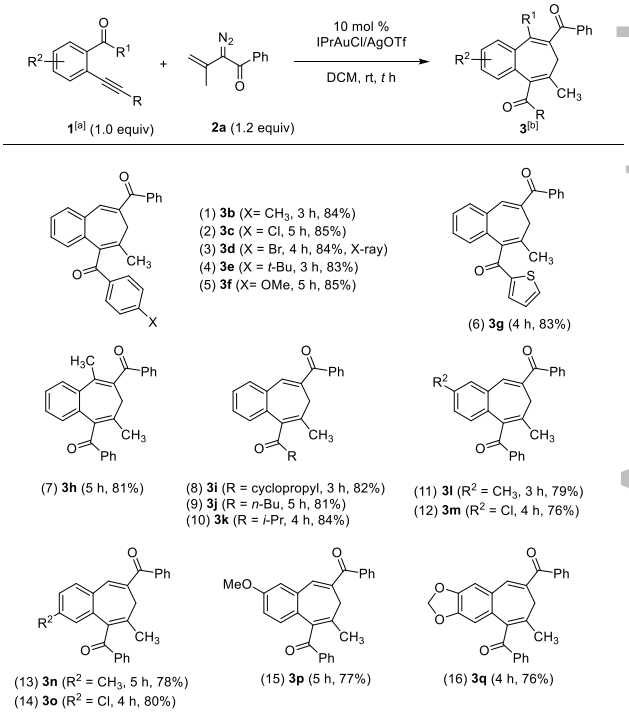
Entry	Catalyst	Solvent	Time (h)	Yield (%)[b]
1	IPrAuCl/$AgSbF_6$[c]	DCM	18	61
2	IPrAuCl/AgOTf	DCM	2	86
3	IPrAuCl/$AgNTf_2$	DCM	21	-
4	LAuCl/AgOTf [d]	DCM	4	63
5[12]	$(PhO)_3PAuCl$/AgOTf	DCM	3	71
6	PPh_3AuCl/AgOTf	DCM	3	77
7	IPrAuCl/AgOTf	DCE	3	83
8	IPrAuCl/AgOTf	MeCN	18	-
9	IPrAuCl/AgOTf	THF	13	-
10[e]	AgOTf	DCM	23	-

[a] **1a** = 0.15M. [b] Product yields are obtained after purification from a silica column, [c] IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene, [d] L = P(*t*-Bu)$_2$(*o*-biphenyl), [e] 82% of the starting alkynal **1a** was recovered in entry 10, Tf = trifluoromethanesulfonyl.

Table 1 shows the optimizations of reaction conditions between 2-alkynylbenzaldehyde **1a** and 2-diazo-3-methyl-1-phenylbut-3-en-1-one **2a** using various gold catalysts. Formation of compound **3a** has been mentioned in our previous work using $(PhO)_3PAuCl$/AgOTf (10 mol %, entry 5).[12] Our initial test with IPrAuCl/$AgSbF_6$ (10 mol %) in DCM at 25 °C (18 h) led to formation of 7*H*-benzo[7]annulene **3a** in 61% (entry 1). IPrAuCl/AgOTf (10 mol %) increased the yield of compound **3a** to 86% yield (entry 2) whereas IPrAuCl/$AgNTf_2$ (10 mol %) afforded products in a complicated mixture (entry 3). Other phosphine gold species such as LAuCl/AgOTf [L = P(*t*-Bu)$_2$(*o*-biphenyl), $P(OPh)_3$ and PPh_3] afforded compound **3a** in 63-77% yields (entries 4-6). For IPrAuCl/AgOTf (10 mol %), the yield of compound **3a** in DCE was 83% (entry 7) whereas MeCN and THF were ineffective for the reactions (entries 8-9). AgOTf alone was entirely catalytically inactive (entry 10). The structure of compound **3a** was inferred from X-ray diffraction of its related **3d**[14] (Table 2, entry 3).

We assessed the substrate scope of these reactions with various 1-acyl-2-alkynylbenzenes **1**; the results are summarized in Table 2. For those aldehyde substrates **1b**-**1f** bearing 4-substituted phenylalkynes (R = 4-XC_6H_4; X = Me, Cl, Br, *tert*-butyl, and OMe), their gold-catalyzed reactions gave the desired products **3b**-**3f** in 83–85% yields (entries 1-5). The molecular structure of **3d** was confirmed with X-ray diffraction.[14] For 2-thienyl substituted analogue **1g**, its corresponding product **3g** formed in 83% yield

Table 2. Scope with various 1-acyl-2-alkynylbenzenes.



[a] **1** = 0.15M. [b] Product yields are obtained after purification from a silica column, Tf = trifluoromethanesulfonyl.

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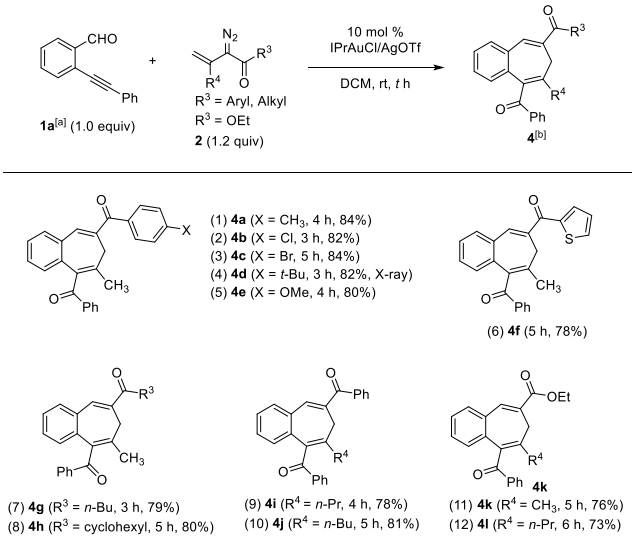
(entry 6). We prepared also 1-acetyl-2-alkynyl benzenes **1h** (R^1 = Me), which proved to be an applicable substrate, further affording compound **3h** in 81% yields (entry 7). The reactions were also amenable to alkyl-substituted alkynes **1i-1k** (R =cyclopropyl, *n*-butyl, and isopropyl), yielding desired **3i-3k** in 81-84% (entries 8-10). We performed the reactions also the 5-phenyl derivatives **1l-1m** (R^2 = Me and Cl), affording compounds **3l-3m** in 79% and 76% yields respectively (entries 11-12). For compounds have substituents at phenyl ring **1n–1o** (R^2 = Me and Cl), their resulting product **3n-3o** were obtained in 78% and 80% yields respectively (entries 13-14). For 4-methoxyphenyl analogue **1p,** its resulting product **3p** was obtained in 77% (entry 15). This [4+3]-annulation is extensible also to dioxolo-substituted benzene **1q**, generating compound **3q** in 76% yield (entry 16).

We further examined these annulations with various 3-alkyl-2-diazo-3-vinyl carbonyls **2**; the results are summarized in Table 3. We prepared 2-diazo-3-vinyl species **2b-2f** bearing varied 4-phenylketone substituents (R^3 = 4-XC_6H_4; X = Me, Cl, Br, *tert*-butyl and OMe); their resulting products **4a-4e** were obtained in satisfactorily yields 80-84% (entries 1-5). The molecular structure of **4d** was confirmed with X-ray diffraction.[14] For 2-thienylketone diazo derivative **2g**, its resulting product **4f** was obtained in 78% yield (entry 6). The reactions were further compatible with alkylketone derivatives **2h** to **2i** (R^3 = *n*-butyl and cyclohexyl), delivering the desired products **4g-4h** in 79-80% yields (entries 7-8). We tested the reactions also on 3-alkyl-2-diazo-3-vinyl ketone as in species **2j-2k** (R^4 = *n*-Pr and *n*-Bu), affording compounds **4i** and **4j** in 78% and 81% yields respectively (entries 9-10). This cycloaddition reaction is extensible to 3-alkyl-2-diazo-3-vinyl esters **2l** and **2m** bearing various 3-alkyl groups (R^4 =

Table 3. Scope with 3-alkyl-2-diazo-3-vinyl carbonyls.

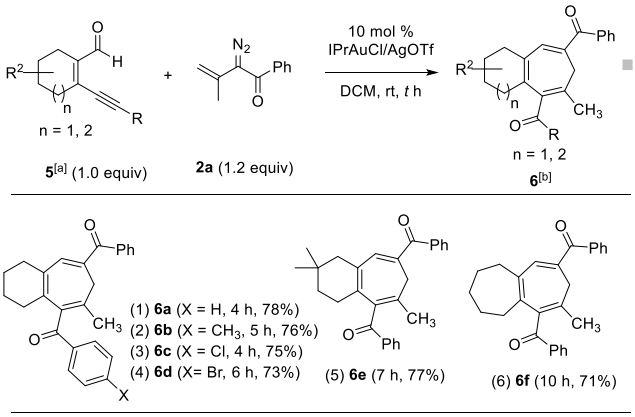


[a] **1a** = 0.15M. [b] Product yields are obtained after purification from a silica column, Tf = trifluoromethane-sulfonyl.

methyl and *n*-propyl), affording compounds **4k** and **4l** in 73%-76% yields (entries 11-12).

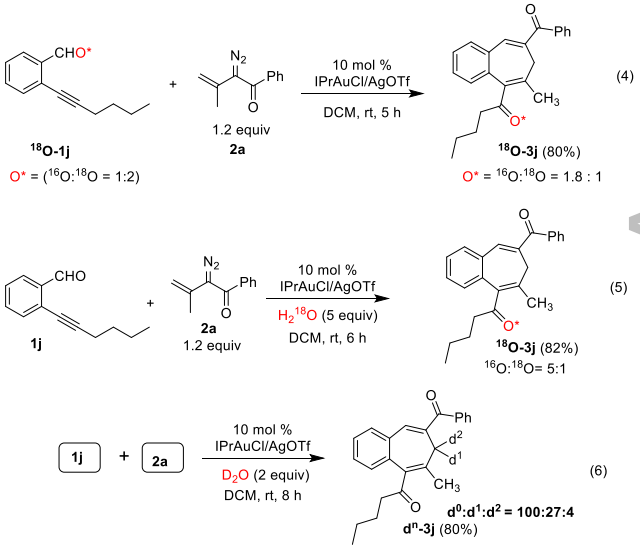
The scope of these reactions was further expanded with its applicability to various nonaromatic enynals **5**; the results are summarized in Table 4. For those cyclohexane bridged enynals **5a-5d** bearing 4-substituted phenylalkynes (R = 4-XC_6H_4; X = H, Me, Cl and Br), their gold-catalyzed reactions provided desired products **6a-6d** in 73-78% yields (entries 1-4). For dimethyl cyclohexane analogue **5e**, its corresponding product **6e** was formed in 77% yield (entry 5). We tested the reactions also on a cycloheptane-bridged enynal **5f,** further affording compound **6f** in 71% yield.

Table 4. Scope with various nonaromatic enynals.



[a] **5** = 0.15M. [b] Product yields are obtained after purification from a silica column, Tf = trifluoromethanesulfonyl.

As shown in scheme 2, we conducted the reactions of 2-diazo-3-methyl-1-phenylbut-3-en-1-one **2a** with species ^{18}O-**1j** bearing 66% ^{18}O-content at its aldehyde; the corresponding product ^{18}O-**3j** contained 36% ^{18}O, indicative a partial loss of ^{18}O (eq 4). We tested the typical reaction also in the presence of $H_2{}^{18}O$; the resulting product O^{18}-**3j** comprised 17% ^{18}O content (eq 5). In these two reactions, we

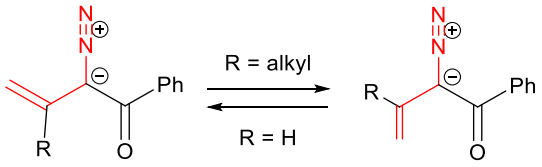


Scheme 2. Isotope labeling experiments.

assigned the ^{18}O position to the alkylketone because its phenyl ketone does not participate in the reaction. In a separate experiment, we added D_2O, which afforded a product in which CH_2 moiety contained no or one deuterium according to the mass analysis (eq 6).

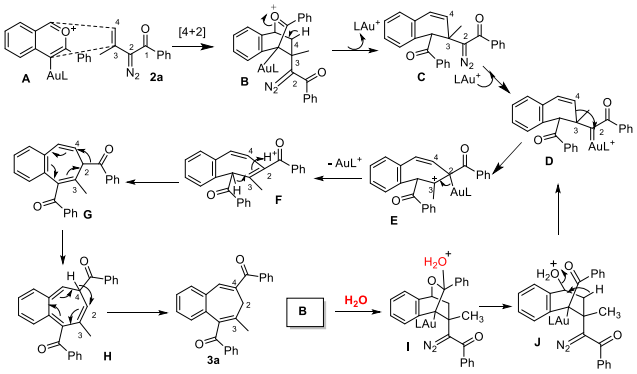
We also used density functional theory (see computational details in the SI) to investigate the effects of 3-alkyl substituents (R = Me versus H) on the U- versus sickle-shaped conformations (Table 5). Three different methods (B3LYP, CAM-B3LYP and M11) all indicate that U-shape is more stable than the sickle-shape by ~2.0 kcal/mol for R = H; but this energy differences become smaller (0.4-0.6 kcal/mol) for R = Me. In other words, sickle conformation is unlikely to form for unsubstituted 2-diazo-2-vinyl ketone (R = H) and the concentration of sickle-shaped conformation will become significant for R = Me.

Table 5. The relative Gibbs free energy for U- and Sickle-shape. The unit for energy is kcal/mol.



R = CH_3	U-shape	Sickle-shape
B3LYP	-0.42	0.00
CAM-B3LYP	-0.59	0.00
M11	-0.53	0.00
R = H		
B3LYP	-2.02	0.00
CAM-B3LYP	-2.06	0.00
M11	-2.06	0.00

Scheme 3 depicts a mechanism to rationalize compound **3a** resulting from gold-catalyzed annulations between benzopyriliums and 2-diazo-3-methyl-1-phenylbut-3-en-1-one **2a**. In this process, gold-containing benzopyriliums **A** undergo [4+2]-cycloadditions with 2-diazo-3-methyl-1-phenylbut-3-en-1-one **2a** to yield species **B** that loses a proton to yield 1,2-dihydronaphthalene species **C**. In the presence of gold catalyst, species **C** becomes gold carbenes **D** to induce an alkene migration to form tertiary carbocations **E** to generate species **F** in which the C-H proton is highly acidic to induce a 1,2-alkene migration. A subsequent 1,7-carbonyl migration[15] of species **G** forms species **H** that undergoes a 1,7-hydrogen migration[16] to yield the observed product **3a.** This main path rationalizes well our HC=^{18}O and D_2O labeling experiments in eqs 4 and 6. In eq 5, we note also that the $H_2{}^{18}O$ also contributes to the oxygen source of the alkyl ketone of compound ^{18}O-**3j.** Accordingly, we postulate that H_2O also attacks oxonium species **B** to form ketal intermediates **I**, then species **J**; this path also yields intermediate **D** to furnish a catalytic circle**.**



Scheme 3. A Plausible reaction mechanism.

In summary, we report gold-catalyzed [4+3]-annulations between benzopyriliums and 3-alkyl-2-diazo-3-vinyl ketones, yielding 7*H*-benzo[7]annulenes efficiently. In this process, the carbon skeletons of the resulting products become rearranged, together with migrations of alkyl and ketone groups. Apart from applicable substrates over a wide scope, these new annulations are applicable to pyrilium intermediates and 3-alkyl-2-diazo-3-vinyl esters, furnishing cycloheptatrienes fused with six- or seven-carbocyclic rings. We performed ^{18}O and ^{2}H isotopic labeling experiments to elucidate the reaction mechanism, which involves an initial [4+2]-cycloadditions of benzopyriliums with 3-alkyl-2-diazo-3-vinyl ketones, followed by formation of gold carbenes to induce a ring expansion, further leading to skeletal rearrangement and substituent migrations.

Experimental Section

Typical procedure for synthesis of (6-methyl-7*H*-benzo[7]annulene-5,8-diyl)bis(phenylmethanone) (3a):

A suspension of IPrAuCl (30 mg, 0.048 mmol) and AgOTf (12 mg, 0.048 mmol) in dry DCM (1 mL) was fitted with N_2 balloon and the mixture was stirred at 25 °C for 5 min. To this mixture was added dry DCM (2 mL) solution of 2-(phenylethynyl)benzaldehyde **1a** (100 mg, 0.485 mmol) and 2-diazo-3-methyl-1-phenylbut-3-en-1-one **2a** (108 mg, 0.582 mmol) at 25 °C. The resulting mixture was stirred for 2 h at 25 °C. The solution was filtered over a short celite bed and evaporated under reduced pressure. The residue was purified on a silica gel column using ethyl acetate/hexane (10:90) as eluent to give compound **3a** as brown oil (151 mg, 0.413 mmol, 86%).

Acknowledgements

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[14] CCDC 1965080 (**3d)** and CCDC 1965081 (**4d)** 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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Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Antony Sekar Kulandai Raj and Rai-Shung Liu*