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Synthesis, Characterization of Spirocyclic λ^3-Iodanes and Their Application to Prepare 4,1-Benzoxazepine-2,5-diones and 1,3-Diynes

Xu Sun,[a,b] Xiao-Qiang Guo,[a] Lian-Mei Chen,*,[a] and Tai-Ran Kang*,[a,b]

Dedication ((optional))

Abstract: *Herein, a [3+2] cycloaddition of aza-oxyallylic cations with EBXs for synthesis of new λ^3-iodanes containing spirocyclic 4-oxazolidinone has been developed. This cyclic λ^3-iodanes display stability in air and excellent solubility in organic solvent. Using them as substrate, both the 4,1-benzoxazepine-2,5-diones and symmetrical 1,3-diynes derivatives were afforded in high yield under copper(I)-catalyzed conditions.*

Hypervalent iodine reagents including iodine (V) (called as λ^5-iodane), iodine(III) (called as λ^3-iodane), iodonium salts and iodonium ylide, show unique reactivity similar to transition metals, and have been widely applied in organic synthesis.[1] Non-cyclic hypervalent iodines are usually unstable (Figure 1 A).[1k] Cyclic hypervalent iodine reagents, such as, 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one (IBX), Dess–Martin periodinane (DMP), benziodoxol(on)es (BXs) and ethynylbenziodoxolones (EBXs), show higher stability than their acyclic analogs due to the inclusion of the iodine atom into a heterocycles (Figure 1 B).[1a, 1k] Therefore, the synthesis and application of cyclic iodanes have gained increasing attention during past decades.[1a, 1k] For example, the cyclic iodine(III) (called as λ^3-iodane) containing acetate, halogens, trifluoromethyl, azides, cyanides, aryl and alkyl groups,[1h, 2] were reported by the pioneering groups, such as, Waser, Zhdankin, Kita, Beringer, Koser, Valvoglis, Moriarty, Ochiai, and Togni.[1,2] More recently, two type of cyclic λ^3-iodanes containing a (diarylmethylene)amino and nitrooxy groups were reported by the group of Kiyokawa, Minakata[2f] and Katayev,[2g] respectively.

The EBXs and modified EBXs have been widely employed as the substrates for the C–alkynyl, heteroatom–alkynyl bond,[3] vinylbenziod-oxoles (VBXs)[4] and heterocycles formation.[5] In the modified EBXs, the carbonyl group or oxygen atom were changed for fine-tuning its reactivity.[6] For example, the carbonyl group of benziodazolone core are replaced by methyl or trifluoromethyl group (Figure 1 B), which were synthesized and applied by the groups of Ochiai,[6a] Zhdankin,[6b] Waser,[6c-f,h] and Itoh.[6i] However, they are difficult to prepare due to the requirement of multistep procedure, Grignard reagents and lithium acetylides.[1a,1h,3,6] In 2019, the oxygen atom was replaced by a nitrogen in the iodoheterocycle of EBXs was synthesized by the group of Waser and coworkers.[6h] Very recently, the EBX−acetonitrile complex was prepared by Tada and coworkers.[6i] Inspired by these works, we were interested in developing a modified EBXs, in which the carbonyl group was replaced with a 4-oxazolidinone ring[7] (Figure 1 B). We believed that the modified EBXs would modulate their steric and electronic environment, and have the potential to introduce amide, ester or alkyl groups into an organic molecule under proper reaction condition. Several examples of [3+2] cycloaddition of azaoxyallyl cation[8] with carbonyl compounds to construct the 4-oxazolidinones motifs were reported in literature.[7] Accordingly, we envisioned that a [3+2] cycloaddition of aza-oxyallylic cation with the carbonyl group of benziodazolone core would undergo to provide a novel spirocyclic λ^3-iodanes containing a spiro-4-oxazolidinones.

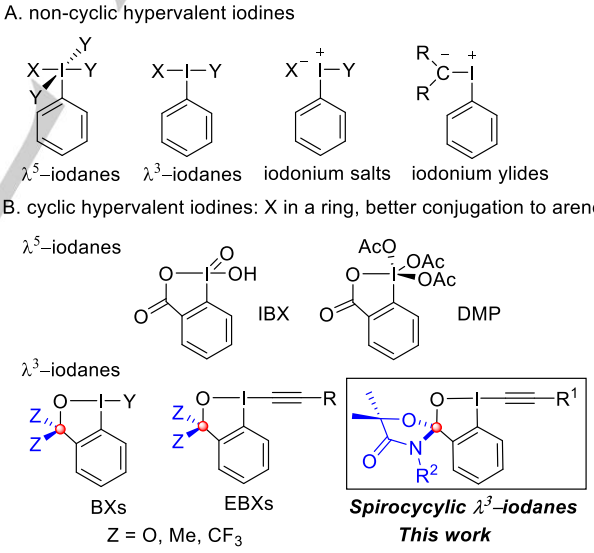

Figure 1. Structure and bonding of hypervalent iodine reagents

The cyclic λ^3-iodanes were applied as versatile electrophilic group-transfer reagents in organic synthesis[2] (Scheme 1 A). As an alkynylated reagent, EBXs have been widely used in an intermolecular alkynylation reaction.[3] For example, EBXs reacted with terminal alkynes to provide 1,3-diynes under gold-catalyzed or *n*BuLi-promoted condition, which were reported by the groups of Liu,[10a] Patil[10b] and Waser,[10c] respectively (Scheme 1 B). The major drawback of these methods is the formation of

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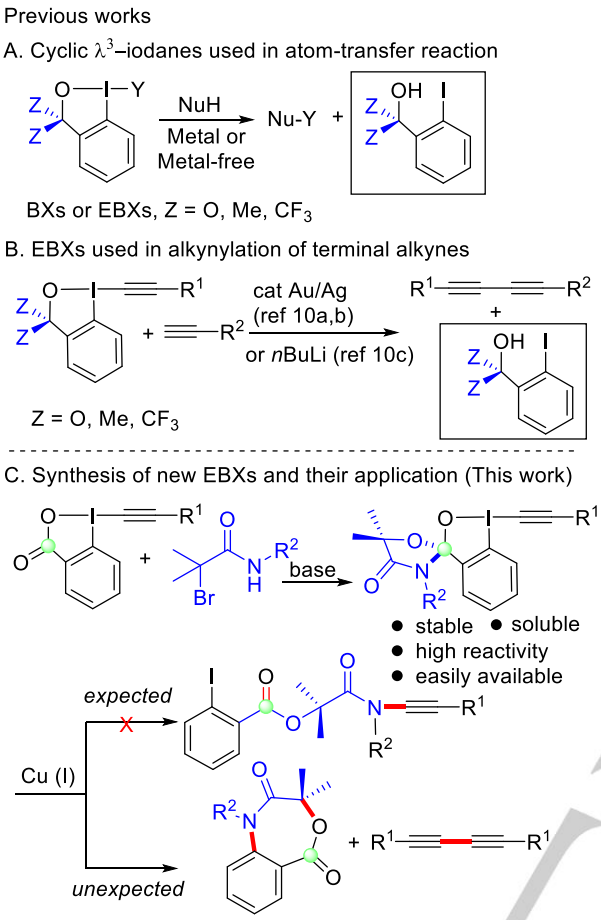
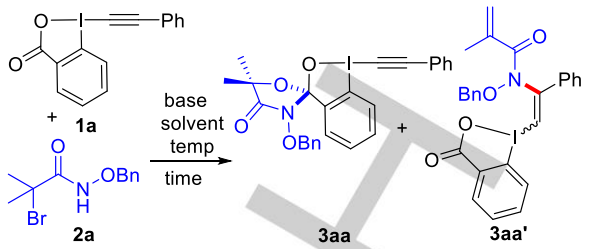
one equivalent of "waste" 2-iodobenzoic acid or (2-iodophenyl)methanol (Scheme 1 A and B).



Scheme 1. Reaction of cyclic λ^3-iodanes.

We initially envisioned that a copper(I)-catalyzed intramolecular rearrangement reaction of the spirocyclic λ^3-iodanes would happen to provide the expected 1-((benzyloxy)(phenylethynyl)-amino)-2-methyl-1-oxopropan-2-yl-2-iodobenzoate (Scheme 1 C). However, the expected product was not obtained, but both the unexpected 4,1-benzoxazepine-2,5-diones and 1,3-diynes were obtained through a sequence bond formation involving C=O, Csp^2–N and Csp–Csp, together with a sequence bond cleavage involving I-O, Csp^2–I and Csp^3–N (Scheme 1 C). Both the 1,3-diynes[11] and 4,1-benzoxazepine-2,5-diones[12] were very valuable compounds. To our knowledge, a strategy for synthesis of both 4,1-benzoxazepine-2,5-diones and 1,3-diynes in one-pot has not been reported so far. Herein, we report that the spirocyclic λ^3-iodanes containing a 4-oxazolidinone ring were synthesized through a [3+2] cycloaddition of aza-oxyallylic cation with EBXs. Both the 4,1-benzoxazepine-2,5-dione and 1,3-diyne derivatives were afforded by copper-catalyzed the spirocyclic λ^3-iodanes.

Table 1. Optimization of reaction conditions.[a]



entry	base	solvent	T (oC)/ time (h)	yield (%) **3aa**[b]	yield (%) **3aa'**[c]
1	Et_3N	TFE	25/12	35	<10
2	Et_3N	HFIP	25/12	40	<10
3	Na_2CO_3	HFIP	25/12	45	<10
4	Na_2CO_3	DCE	25/12	70	15
5	K_2CO_3	DCE	25/2	75	15
6	Cs_2CO_3	DCE	25/2	85	10
7	Cs_2CO_3	DCE	0/12	45	45b
8	Cs_2CO_3	DCE	-20/12	50	45b
9	Cs_2CO_3	DCE	60/2	60	<10

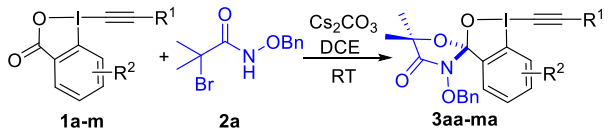
[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), base (0.3 mmol, 3.0 equiv) in 0.5 mL solvent. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis of the reaction crude reaction mixture.

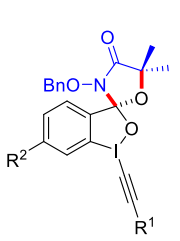
At the outset of our studies, we chose EBX (**1a**) and N-(benzyloxy)-2-bromo-2-methylpropanamide (**2a**) as a model system to optimize the reaction conditions, and the screening results are summarized Table 1. Considering the stabilization of azaoxyallyl cation in fluorinated solvents, the hexaflfluoro-2-propanol (HFIP) and 2,2,2-trifuoroethanol (TFE) were employed as solvent. NEt_3 and Na_2CO_3 were employed as bases for the reaction.[7,8] However, **3aa** was afforded only in low yields (35-45%) for 12 h, and the byproduct nitrogen-substituted VBX **3aa'** (see SI for details) was trace (entries 1-3). When 1,2-dichloroethane (DCE) was employed as solvent, the desired product **3aa** was afforded in 70% yield, and the byproduct **3aa'** was afforded in 15% yield (entry 4). Using K_2CO_3 and Cs_2CO_3 as base, the yield of **3aa** increased to 75% and 85% for 2 hours, along with 15% and 10% yield of **3aa'**, respectively (Table 1, entries 4-6). Therefore, Cs_2CO_3 was the best choice (entry 6). Lowing or raising the reaction temperature, the unsatisfactory results were obtained (entries 7-9).

With the optimal reaction conditions established, we next explored the substrate scope. A wide range of cyclic λ^3-iodanes containing spiro-4-oxazolidinones were prepared, as shown in Scheme 2. When R^1 was phenyl group, the substituents at the *para*, *meta*, or *ortho* positions of phenyl ring, and the substrates containing a variety of functional groups including methyl (**1b**, **1d**), halogens (**1c, 1e**), phenyl (**1f**) and ester (**1g**) exhibited good results, affording the cyclic λ^3-iodanes **3aa−3ga** in moderate to good yields (66%−85%). However, when R^1 was alkyl group (Et or cyclohexyl), the desired product did not obtain

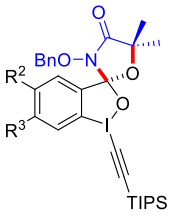
due to the mess of reaction. When R^2 was Cl group, the product **3ha** was afforded in 68% yield. To our gratification, when R^1 was TIPS, various substituents at the benziodazolone core (R^2 = H, Me, F, NO_2 and R^3 = Cl) (**1i-m**) were tried, providing the λ^3-iodanes (**3ia, 3ja, 3ka, 3la, 3ma)** in excellent yields (90-96%).

Scheme 2. Scope of ethynylbenziodoxol(on)es.[a,b]





R^2 = H, R^1 = C_6H_5, **3aa** 85%
2-MeC_6H_4, **3ba** 78%
2-BrC_6H_4, **3ca** 66%
3,4-$(Me)_2C_6H_3$, **3da** 82%
3-ClC_6H_4, **3ea** 68%
4-PhC_6H_4, **3fa** 75%
4-$(CO_2Et)C_6H_4$, **3ga** 75%
R^1 = Et or cyclohexyl, mess
R^1 = Ph, R^2 = Cl, **3ha** 68%



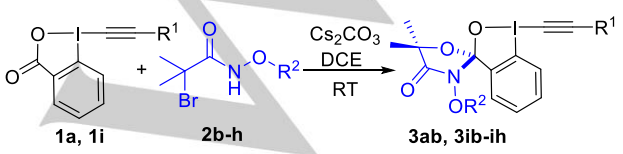
R^3 = H, R^2 = H, **3ia** 94%
Me, 3**ja** 96%
F, 3**ka** 92%
NO_2, 3**la** 91%
R^2 = H, R^3 = Cl, **3ma** 90%

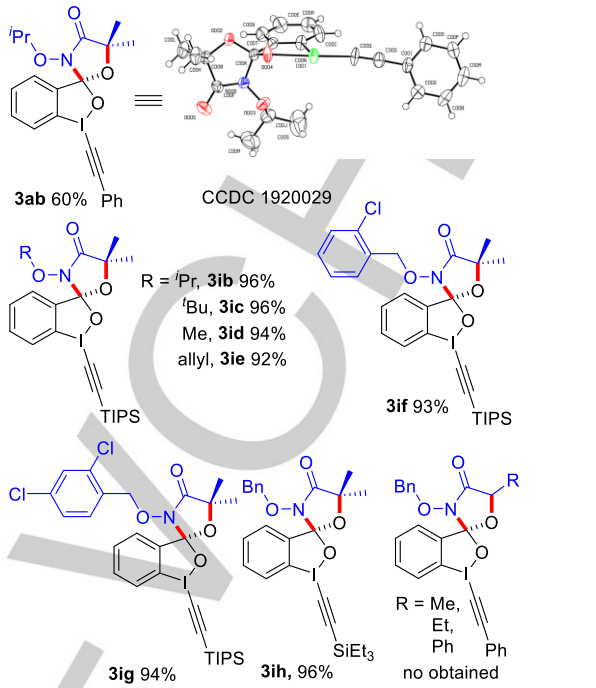
[a] Reaction conditions: **1a-m** (0.1 mmol, 1 equiv), **2a** (0.15 mmol, 1.5 equiv), Cs_2CO_3 (0.3 mmol, 3.0 equiv) in 0.5 mL 1,2-dichloroethane for 2-6 h at room temperature. [b] Isolated yield.

The scope of α-halohydroxamates was also examined (Scheme 3, **2b-h**). Replacing the benzyl group with isopropyl (**3ab**, **3ib**), *tert*-butyl (**3ic**), methyl (**3id**), allyl (**3ie**) and halogen substiuted benzyl (**3if**, **3ig**) groups worked well. It was found that the reactivity of the silyl substituents was better than that of phenyl group on the cyclic λ^3-iodanes. For example, **3ab** (R^1 = Ph) was obtained in 60% yield, and **3ib−ig** (R^1 = TIPS) were obtained in excellent yields (92-96%). When R^1 was triethyl silyl group, the desired product **3ih** was afforded in 96% yield. However, the monomethyl, monoethyl, and monophenyl-substituent on α-halohydroxamates failed to provide the desired products, and only the corresponding byproducts (VBXs) were obtained in almost quantitative yields.

It should be noted that all these cyclic λ^3-iodanes (**3aa-ma, 3ab,** and **3ib-ih**) display stable in air and have excellent solubility in common organic solvents, such as DMF, methanol, chloroform, dichloromethane, and acetonitrile. The structure of **3ab** was confirmed by single crystal X-ray analysis (see SI for details).

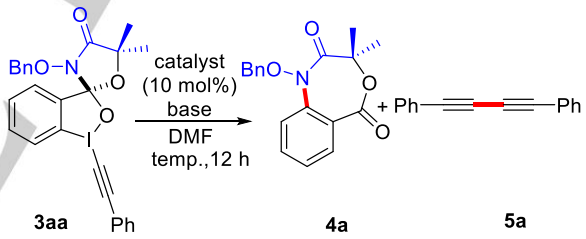
Scheme 3. Scope of of α-halohydroxamates.[a,b]





[a] Reaction conditions: **1a** or **1i** (0.1 mmol, 1.0 equiv), **2b-h** (0.15 mmol, 1.5 equiv), Cs_2CO_3 (0.3 mmol, 3.0 equiv) in 0.5 mL 1,2-dichloroethane for 2-6 h at room temperature. [b] Isolated yield.

Table 2. Optimization of reaction conditions[a]



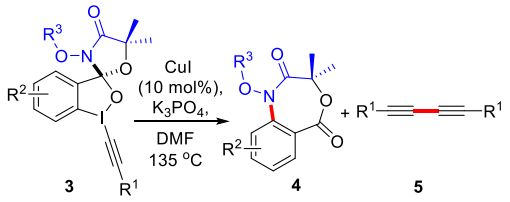
entry	catalyst	base	T (°C)/t (h)	**4a** yield (%)[b]	**5a** yield (%)[c]
1	-	-	135/12	-	-
2	CuCl	K_3PO_4	135/12	85	95
3	CuBr	K_3PO_4	135/12	90	98
4	CuI	K_3PO_4	135/12	92	99
5	CuI	K_2CO_3	135/12	40	90
6	CuI	K_3PO_4	90/12	60	95

[a] Reaction conditions: **3aa** (0.1 mmol, 1.0 equiv), catalyst (10 mol%), base (0.1 mmol, 1.0 equiv) in 0.5 mL DMF. [b] Isolated yield. [c] Isolated yield.

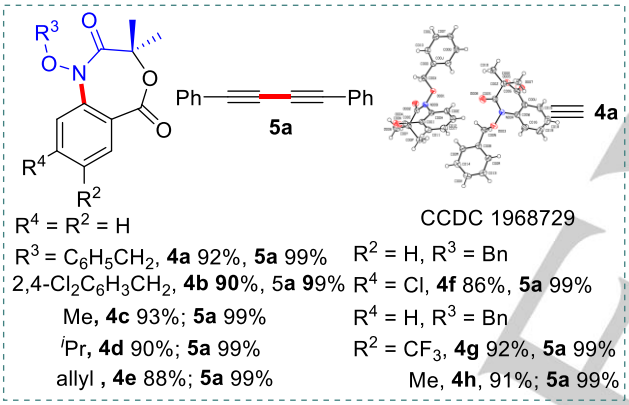
We switched our focus toward exploring their application, as shown in Table 2. We chose **3aa** as model substrate to optimize the reaction conditions. Without copper catalyst and base, heating **3aa** in DMF at 135 °C, no new product was observed on the thin layer chromatography (TLC) for 12 h (Table 2, entry 1). This observation suggests that **3aa** is stable in DMF at high temperature. When **3aa** was treated in the presence of CuCl and K_3PO_4 as the catalytic system in DMF at 135 °C, **4a** and **5a** were

afforded in 85% and 95% yield, respectively (entry 2). The expected copper(I)-catalyzed an intramolecular rearrangement reaction didn't happen. Therefore, the expected product 1-((benzyloxy)(phenylethynyl)-amino)-2-methyl-1-oxopropan-2-yl-2-iodobenzoate compound wasn't obtained (See SI for details). And then, various copper(I) and bases were examined (entries 3-5). The best result was obtained with CuI and K_3PO_4 as catalytic system, giving 4,1-Benzoxazepine-2,5-dione **4a** in 92% yield and 1,3-diyne **5a** in 99% yield (entry 4). The lower yield of **4a** was afforded if K_2CO_3 is used as base (entry 5). Lowering the temperature from 130 °C to 90 °C, the yield of **4a** reduced to 60% (entry 6).

Scheme 4. Scope of cyclic λ^3-iodanes.[a,b]



■ synthesis of **4a-h** and **5a**

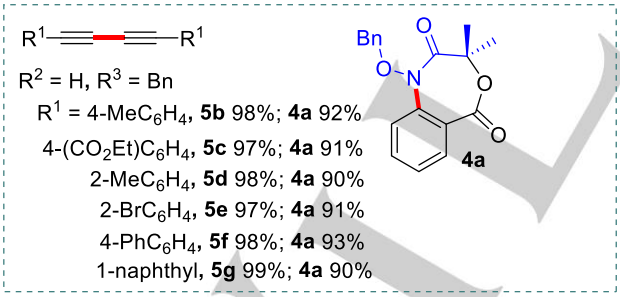


$R^4 = R^2 = H$

$R^3 = C_6H_5CH_2$, **4a** 92%, **5a** 99%
2,4-$Cl_2C_6H_3CH_2$, **4b** 90%, 5a 99%
Me, **4c** 93%; **5a** 99%
^{i}Pr, **4d** 90%; **5a** 99%
allyl , **4e** 88%; **5a** 99%

R^2 = H, R^3 = Bn
R^4 = Cl, **4f** 86%, **5a** 99%
R^4 = H, R^3 = Bn
$R^2 = CF_3$, **4g** 92%, **5a** 99%
Me, **4h**, 91%; **5a** 99%

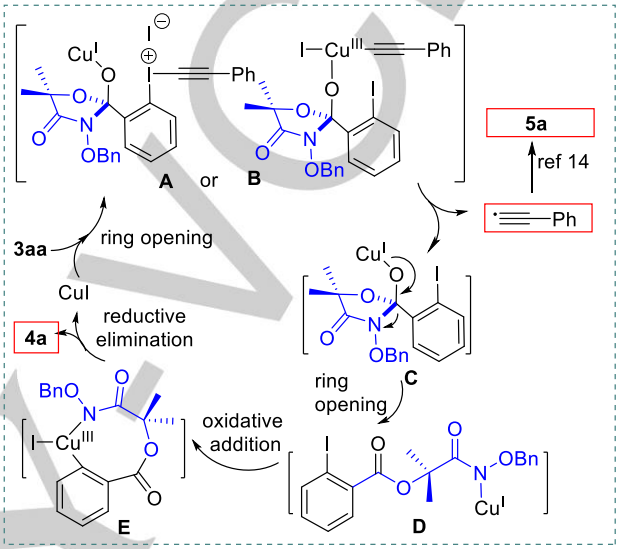
■ synthesis of **4a** and **5b-g**



R^2 = H, R^3 = Bn
R^1 = 4-MeC_6H_4, **5b** 98%; **4a** 92%
4-$(CO_2Et)C_6H_4$, **5c** 97%; **4a** 91%
2-MeC_6H_4, **5d** 98%; **4a** 90%
2-BrC_6H_4, **5e** 97%; **4a** 91%
4-PhC_6H_4, **5f** 98%; **4a** 93%
1-naphthyl, **5g** 99%; **4a** 90%

[a] Reaction conditions: **3** (0.1 mmol, 1 equiv), CuI (10 mmol%), K_3PO_4 (0.1 mmol, 1.0 equiv) in 0.5 mL DMF for 12h at 135°C. [b] Isolated yield.

We next explored the substrate scope under the optimized reaction conditions. A wide range of both the 4,1-benzoxazepine-2,5-diones **4a-h** and 1,3-diynes **5a-g** were shown in Scheme 4. When R^3 were chlorine group substituted benzyl (**4b**), methyl (**4c**), isopropyl (**4d**) and allyl (**4e**), it led to give the corresponding 4,1-benzoxazepine-2,5-diones in 88-93% yields and 1,3-diyne **5a** in almost quantitative yields. When R^2 was CF_3 and Me group, it gave the similar results. Pleasingly, using various groups on the aryl ring (R^1), the corresponding 1,3-diynes, including methyl (**5b, 5d**), ester (**5c**), bromine (**5e**), phenyl (**5f**) and 1-napthyl (**5g**) group were obtained in quantitative yields, and the 4,1-benzoxazepine-2,5-dione **4a** was also obtained in excellent yields (90-93%). When R^1 were alkyl group, the corresponding 1,3-diyne and the 4,1-benzoxazepine-2,5-diones were not obtained. The structure of **4a** was confirmed by single crystal X-ray analysis (see SI for details).



Scheme 5. Proposed speculative mechanism.

We propose a possible reaction mechanism in Scheme 5. The copper(I) catalyst activates cyclic λ^3-iodane **3aa**[1a,13] to form the iodonium salt **A** or the copper(III) complex **B** by a ring opening.[1a,13] Both **A** and **B** would transform directly to copper(I) complex **C**, iodine radical and alkyne radical intermediate. The symmetrical 1,3-diyne **5a** can be formed via a homocoupling of alkyne radical.[14] The copper(I) complex **C** undergoes a ring opening to form copper(I) complex **D,** which followed to produce copper(III) complex **E** *via* an oxidative addition process. The desired product **4a** and the initial copper (I) catalyst were obtained from the copper (III) complex **E** by a reductive elimination process.

In summary, we have developed a (3+2)-cycloaddition reaction between EBXs and azaoxyallyl cations to afford a spirocyclic λ^3-iodines bearing a 4-oxazolidinone ring. The cyclic λ^3-iodines is structurally characterized by X-ray analysis and displays satisfactory solubility and stability in solution as well as in the solid state. Using them as precursors, both the 4,1-benzoxazepine-2,5-diones and symmetrical 1,3-diynes were obtained under a copper(I)-catalyzed condition. The potential applied research on the spirocyclic λ^3-Iodines and the 4,1-benzoxazepine-2,5-diones are ongoing in our group.

Acknowledgements

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Keywords: hypervalent iodine reagents • azaoxyallyl cations • benzoxazepinediones • 1,3-diynes • copper

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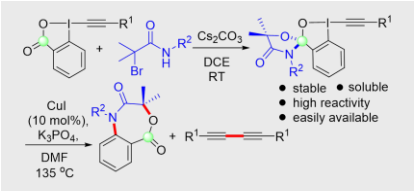
The spirocyclic hypervalent iodine reagents containing 4-oxazolidinone ring are prepared *via* a (3+2)-cycloaddition of azaoxyallyl cations with EBXs. They display satisfactory stability and solubility in organic solvents. Using them as precursors, both 4,1-benzoxazepine-2,5-diones and 1,3-diynes derivatives were afforded in one-pot under copper (I)-catalyzed conditions.



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Synthesis, Characterization of Spirocyclic λ^3-Iodanes and Their Application to Prepare 4,1-Benzoxazepine-2,5-diones and 1,3-Diynes