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Eosin Y- and Copper-Catalyzed Dark Reaction To Construct Ene-γ-Lactams

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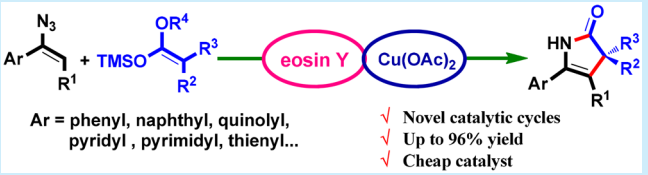
Supporting Information

ABSTRACT: Eosin Y, a common organo-photocatalyst in visible-light photoredox processes, was found to show excellent catalytic activities for thermal redox reactions under a catalytic amount of $Cu(OAc)_2$. With this catalytic system, vinyl azides and ketene silyl acetals combine to form formal [3 + 2] cycloadducts by α-ester radical addition without light irradiation. This method provides a mild and straightforward paradigm to prepare important synthons of five-membered ene-γ-lactams and bridge ring lactams. It is the first example of an eosin Y-catalyzed redox reaction in the dark.



Ene-γ-lactams are significant synthons as they are widely used in synthesis and key structural elements in a wide range of bioactive natural products and medicinally relevant compounds.[1] They could be transformed into chiral lactams that are ubiquitous pharmacophore motifs by asymmetric hydrogenation.[2] As a highly versatile intermediate, the electron-rich enamine scaffolds of ene-γ-lactams could participate in hetero-Diels−Alder reaction[3] or [3 + 2] cyclization with α, β-unsaturated carbonyl compounds, providing tetrahydropyranopyrrolones or enantioenriched bicyclic γ-lactams.[4] They could also react with electrophilic aldehydes to afford the fused bicycles.[4a] In addition, ene-γ-lactams could be activated by appropriate Brønsted or Lewis acid via in situ formed *N*-acyliminium ions; further reaction of the iminium motifs with proximal nucleophiles produces various valuable nitrogen-bearing polycycles.[5]

Accordingly, several synthetic strategies for accessing ene-γ-lactams have been developed. In 1960s, Wasserman and Moon[6] reported the synthesis of ene-γ-lactams through an oxidative rearrangement of poly-substituted pyrroles. It is known that ene-γ-lactams can be obtained from anhydrides in four steps. Specifically, Vassilikogiannakis and co-workers[3−5] explored an "all-in-one" reaction sequence to produce ene-γ-lactams from the reaction of singlet oxygen with furans followed by treatment with Me_2S and primary amines. In these transformations, most of the approaches require multistep reactions to prepare the precursors or access the products.[2a,7] Therefore, a concise, efficient and straightforward transformation from readily available materials to ene-γ-lactams under mild reaction conditions is highly desirable.

In conjunction with our efforts aimed at extending the utility of α-carbonyl radical chemistry,[8] we describe an intramolecular redox strategy to prepare ene-γ-lactams from vinyl azides[9] and ketene silyl acetals (KSAs).[10] We propose that both reaction partners might be activated simultaneously by a redox catalytic cycle to afford the desired [3 + 2] cycloadducts. In order to realize this idea, a simple but novel eosin Y/$Cu(OAc)_2$ catalytic system was found to drive the cyclization without light irradiation. Eosin Y is widely employed as a cheap, readily accessible, and green photocatalyst in visible-light photoredox catalysis, however its catalytic potential in thermal reaction is still unexploited.

Our initial effort was focused on visible-light photoredox catalysis because both vinyl azides and KSAs should be easily activated by an organic dye-mediated photoredox cycle. However, accompanied by the products of the desired ene-γ-lactams, 2*H*-azirines were always obtained via an energy transfer process (Scheme 1c).[9c,11] After realizing that the process is inevitable under light irridiation, we turned to devising an organic dye-redox system that could catalyze the formal [3 + 2] cyclization in the dark. Due to a large part of xanthenes dyes in oxidative state having the potential to oxidize KSAs,[12] we anticipated that the combination of a xanthene with a proper cocatalyst would drive the dye based redox cycle, leading to the desired ene-γ-lactams without the formation of 2*H*-azirines.

To validate this idea, our initial studies focused on the [3 + 2] cyclization of α-phenyl vinyl azide **1a** with KSA **2a** at room temperature. After extensive screening (see the Supporting Information), we were delighted to observe that the reaction of **1a** with **2a** in CH_3CN solution containing catalytic eosin Y (3 mol %) and $Cu(OAc)_2$ (5 mol %) provided the respective ene-γ-lactam **3a** in 96% yield. Control experiments established that both eosin Y and $Cu(OAc)_2$ were necessary for an efficient reaction. Meanwhile, when a series of xanthenes dyes and

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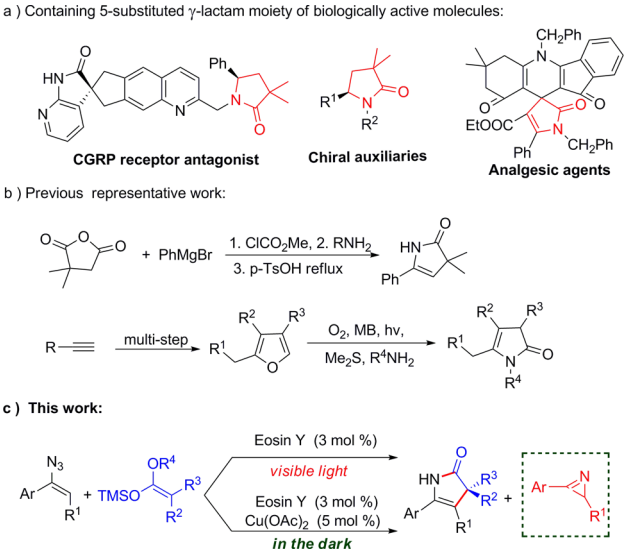
Scheme 1. Method of Constructed Ene-γ-lactams



carboxylate ligands was screened, the product **3a** was obtained in unsatisfactory yields, which indicated eosin Y plays an irreplaceable role in the catalytic system.

With optimized conditions in hand, we evaluated the scope of the vinyl azide component, utilizing **2a** as the common KSA partner. As shown in Figure 1, various substituted α-aryl vinyl azides worked well to deliver the corresponding annulated products in good to excellent yields. Among all the examples presented, it was found that the electronic property slightly affected the product yields. α-Aryl vinyl azides bearing an electron-donating substituent on the phenyl motifs afforded lower yields than those with electron withdrawing groups in most cases. The absolute configuration of **3a** was unambiguously confirmed by single-crystal X-ray diffraction analysis. Many versatile functional groups, such as methoxyl (**3b**), halides (**3c**, **3d**), alkyl (**3e**), formyl (**3f**), phenyl (**3g**), trifluoromethyl (**3h**), vinyl (**3i**), esters (**3j**) or others, were all suitable in this transformation, highlighting the potential of the method in organic synthesis. Substitution at the ortho and meta positions of the phenyl ring was successfully incorporated as well (**3k**–**3m**, 65%–94%). Subsequently, the transformation proceeded well with various polyaromatic and heteroaryl-substituted vinyl azides to deliver the corresponding γ-ene-lactams, such as naphthyl (**3n**), quinolyl (**3p**), pyridyl (**3q**), pyrimidyl (**3r**), and thienyl (**3s**). Moreover, 4,5-disubstituted γ-ene-lactams can be also obtained from α-phenyl β-ethoxycarbonyl vinyl azide in good yield (**3t**, 62%). It is worth noting that certain vinyl azides are beyond the reach of the present catalytic systems such as **1u**–**1x**.

We next turned our attention to the capacity of KSAs to participate in [3 + 2] cycloaddition to synthesize γ-ene-lactams (Table 1). We found that the alkoxyl group (**2b**–**2c**) of KSA had less affect on the reactivity and the yield of the product (85%–87%). The β,β-asymmetrically disubstituted KSA also proceeded smoothly under the standard conditions (**3u**, 79%). To further explore the advantage of the dye-catalyzed [3 + 2] cycloaddition, the exocyclic KSAs were evaluated under the standard conditions. Delightfully, the reactions proceeded well and delivered spirocyclic lactams 2-azaspiro[4.5]dec-3-en-1-ones in good yields (**3v**–**3w**, 72%–75%). In addition, the exocyclic KSAs **2g** can be utilized as an effective substrate for

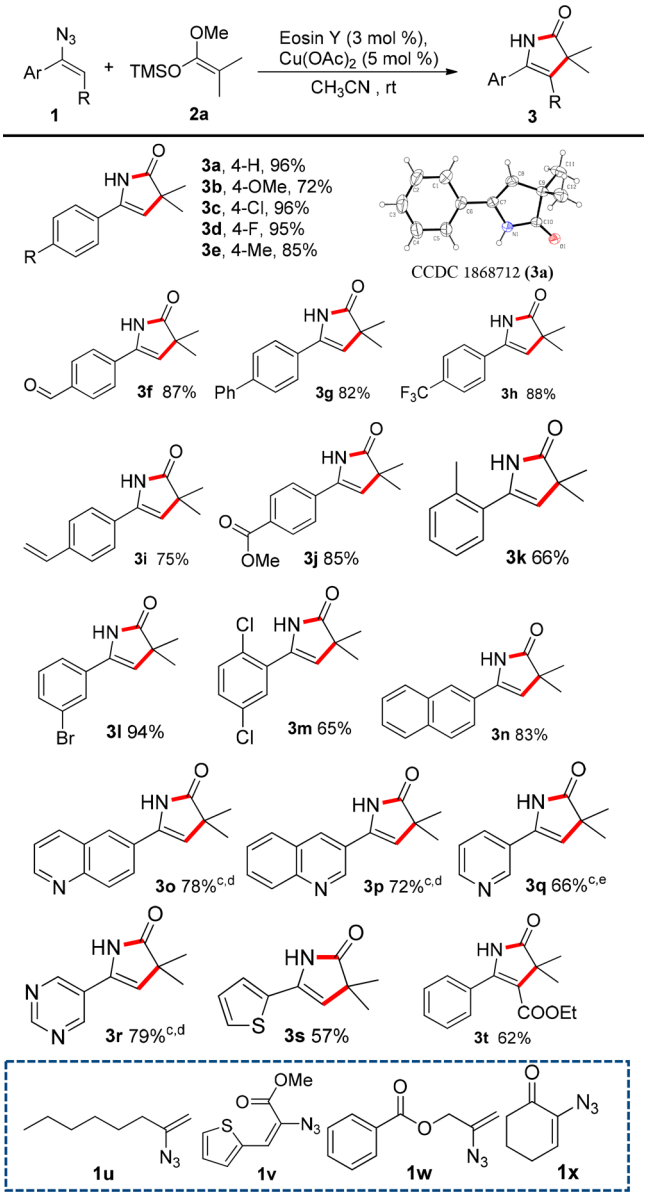


Figure 1. Scope of vinyl azides. (a) Conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), eosin Y (3 mol %), $Cu(OAc)_2$ (5 mol %) in 1.0 mL of dry CH_3CN under an argon atmosphere for 12 h at room temperature. (b) Isolated yields. (c) Reaction heated to 60 °C. (d) For 36 h. (e) For 48 h.

this cyclization, producing nonplanar and hard-earned bicyclic lactams 2-oxa-7-azabicyclo [3.2.1] octan-6-ones in good yield (**3x**–**3y**, 69%–77%).[13] However, the monosubstituted KSA did not provide the desired ene-γ-lactams.

Ene-γ-lactams are versatile synthetic intermediates and could be further converted to various compounds (Scheme 2).[4−6] For example, the asymmetric hydrogenation of **3a** successfully delivered chiral γ-lactam **10**[14] in excellent yield and enantioselectivity.[2a] Moreover, the reduction of **3a** using lithium aluminum hydride provided 1-pyrroline **7** in 72% yield. Furthermore, the thiocyanation of **3a** with potassium thiocyanate and iron tribromide was carried out to afford β-thiocyanted ene-γ-lactam **9** in excellent yield.[15]

Finally, by using a polypyridyl iridium(III) catalyst ($Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$), the ene moiety of γ-lactam **3a** easily underwent visible-light driven intramolecular [2 + 2] cyclo-

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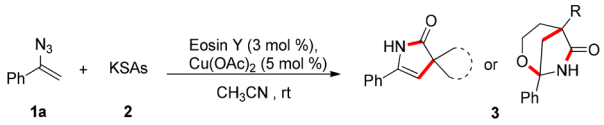
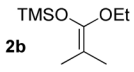
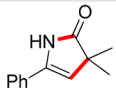
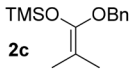
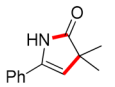
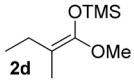
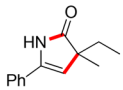
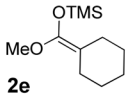
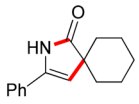
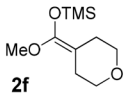
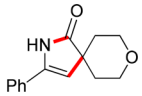
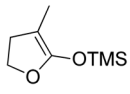
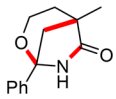
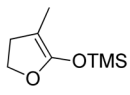
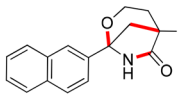
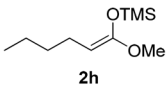
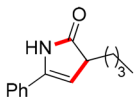
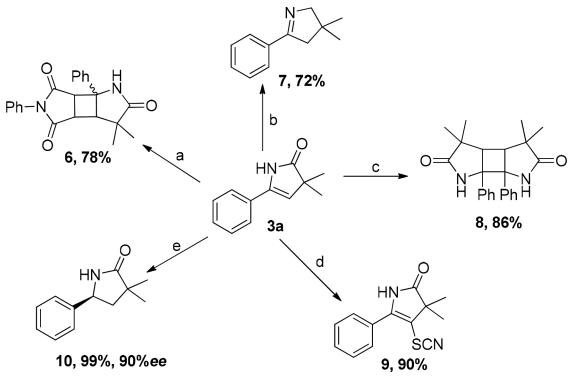
Table 1. Scope of Ketene Silyl Acetals[a]



entry	KSAs	products	3 (%)[b]
1	 2b		**3a**, 85%
2	 2c		**3a**, 87%
3	 2d		**3u**, 79%
4	 2e		**3v**, 75%[c]
5	 2f		**3w**, 72%
6	 2g		**3x**, 77%
7	 2g		**3y** 69%[c,d]
8	 2h		**3z**, 0%

[a]Conditions: **1a** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv), eosin-Y (3 mol %), $Cu(OAc)_2$ (5 mol %) in 1.0 mL of dry CH_3CN under an argon atmosphere for 12 h at room temperature. [b]Isolated yields. [c]**2** (0.3 mmol, 3.0 equiv). [d]48 h.

Scheme 2. Synthetic Applications of Compound 3a[a]

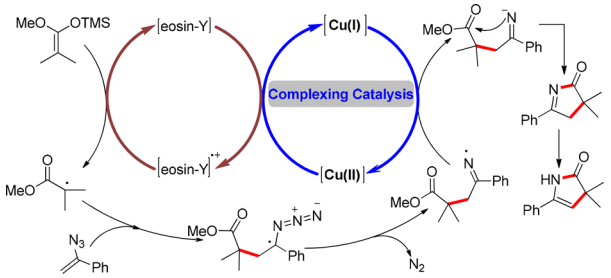


[a]Conditions: (a) (1 mol %) $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$; (2.0 equiv) *N*-phenylmaleimide in anhydrous CH_3CN irradiation with LEDs at 455 nm; (b) (3.0 equiv) $LiAlH_4$ in THF 70 °C; (c) $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1 mol %) in anhydrous CH_3CN irradiation with LEDs at 455 nm; (d) (0.5 equiv) $FeBr_3$, (2.0 equiv) KSCN in CH_3CN 80°C; (e) ref 2a.

addition or crossed [2 + 2] cycloaddition with *N*-phenylmaleimide to form cyclobutanes **6** or **8** in high yields.[16]

Although a detailed mechanism of the eosin Y-catalyzed cyclization is beyond the scope of this paper, Scheme 3

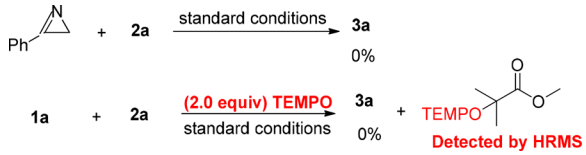
Scheme 3. Proposed Pathway of Ene-γ-Lactams



outlines a mechanistic picture on the basis of the above results and further control experiments (see below). Thus, the initial reaction between eosin Y and the $Cu(OAc)_2$ would afford the eosin Y radical cation,[3b] which would be capable of oxidizing the KSAs via singlet electron transfer (SET) to α-ester radicals. Addition of α-ester radicals to vinyl azides would produce the iminyl radical with dinitrogen.[9a] The resulting iminyl radicals then should be reduced by low-valent Cu(I), thus affording the desired iminyl anions and regenerating Cu(II).[9b] Finally, intramolecular nucleophilic substitution of the iminyl anion moiety to ester followed by isomerization delivers the final products.

We inferred the existence of an α-ester radical intermediate because of the evidence provided by the radical trapping experiment. The reaction can be fully suppressed when 2.0 equiv of TEMPO was added and the mixture was studied by HRMS. The trapped peak was detected at 258.2062 in accordance with calculation (see Scheme 4). We also

Scheme 4. TEMPO Trapping and Control Experiment



conducted a spin trapping experiment using 5,5-dimethylpyrroline *N*-oxide (DMPO) and observed the formation of persistent nitroxide radical adduct with ESR spectroscopy (see the Supporting Information). However, 2*H*-azirine, an important intermediate of vinyl azide chemistry, could not produce ene-γ-lactams **3a** in standard conditions.

It is worth noting that equivalent $Cu(OAc)_2$ could not solely drive the [3 + 2] cycloaddition at room temperature. The oxidation potential of KSAs is around 0.90 V (vs SCE),[10a] which is much higher than the reduction potential of $Cu(OAc)_2$ (≈0.32 V vs Fc^+/Fc),[17] suggesting that the electron transfer from $Cu(OAc)_2$ to KSAs is thermodynamically unfavorable. Therefore, the existence of eosin Y is crucial for the cyclization.

Although the attempt to detect the short-lived eosin Y radical cation[18] in the mixture of eosin Y and $Cu(OAc)_2$ failed at this moment, the formation of Cu(I) was verified by X-ray photoelectron spectroscopic (XPS) measurements. Upon analysis of the mixture of $Cu(OAc)_2$ and eosin Y, XPS

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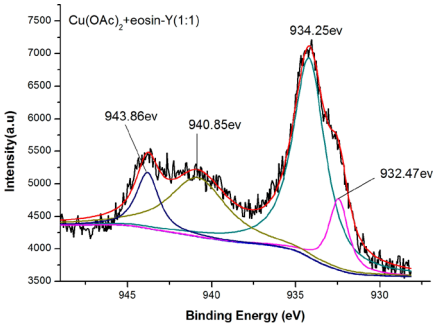
detected the peak characteristic of Cu(I) at 932.5 eV (see Scheme 5).[19] We found that the maximum absorption peak of

Scheme 5. X-ray Photoelectron Spectrum



eosin Y was increased and slightly blue-shifted with progressive addition of $Cu(OAc)_2$ and a new reduction peak at 0.88 V was detected in acetonitrile solution containing $Cu(OAc)_2$ and eosin Y by cyclic voltammograms; this may contribute to the chelation between copper(II) ions and the eosin Y (see the Supporting Information). Meanwhile, the chelation has also been detected by FTIR. The 1752.19 cm^{-1} resonance (carbonyl group) of eosin Y disappeared with the addition of $Cu(OAc)_2$ (see the Supporting Information). Thus, it is plausible that Cu(I) and the eosin Y radical cation could simultaneously arise from the inner-sphere electron transfer of the $Cu(OAc)_2$−eosin Y complex.[20]

Xanthenes dyes have been widely used as organo-photocatalysts in visible-light driven synthetic transformations.[12,21] In stark contrast, the redox abilities of these dyes in the ground state were greatly ignored. The newly developed eosin Y−$Cu(OAc)_2$ system allows the [3 + 2] cyclization of vinyl azides with KSAs and reveals real-world practical advantages compared to the eosin Y based photoredox system, such as the photo byproducts 2*H*-azirines are no longer produced. With this system, the desired ene-*γ*-lactams were obtained smoothly at room temperature. It is also the first report on exploring xanthene dyes as the redox catalyst in thermal reactions. Further expansions of dye-catalyzed thermal reactions and full disclosure of the mechanism are now in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03147.

Detailed experimental procedures, characterization of new compounds, UV−vis, IR, XPS, and NMR spectra, and CVs (PDF)

Accession Codes

CCDC 1868712 (**3a**) 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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