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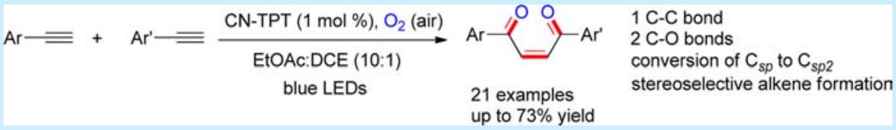
Visible-Light-Mediated Oxidative Dimerization of Arylalkynes in the Open Air: Stereoselective Synthesis of (*Z*)-1,4-Enediones

Donglei Wei[‡] and Fushun Liang[*,†]

[†]College of Chemistry, Liaoning University, Shenyang 110036, China

[‡]Department of Chemistry, Northeast Normal University, Changchun 130024, China

Supporting Information



ABSTRACT: An organic photoredox catalytic one-pot protocol is developed for the highly stereoselective synthesis of (*Z*)-1,4-enediones. The reaction starts directly from alkyne precursors, using 4-(4-cyanophenyl)-2,6-diphenylpyrylium tetrafluoroborate (CN-TPT) as an efficient photosensitizer and dioxygen in the air as a green oxidant. A $C_{sp}-C_{sp}$ oxidative coupling/[4 + 2] cyclization (with dioxygen)/fragmentive isomerization cascade mechanism was proposed. The predominant formation of (*Z*)-1,4-enediones is attributed to the efficient visible-light illumination from blue LEDs, along with possible energy transfer from the photosensitizer CN-TPT to the *E*-isomers.

1,4-Enediones constitute a key structural motif of many bioactive compounds including steroids, antitumor agents, and marine natural products.[1] They may also serve as important synthons in the construction of various heterocycles such as furans, pyrroles, thiophenes, pyrazines, hydantoins, isoxazoles, and indolizines.[2] Synthetic methods toward 1,4-enediones include coupling of methyl ketones,[3a−c] oxidative ring opening of furan and thiophene derivatives,[3d−g] oxidation of α,β-enones,[3h] oxidative rearrangement of 2-alkynyl alcohols,[3i] oxidation of 3-en-1-ynes,[3j] oxidative dimerization of alkynes,[3k,l] and Wittig reactions.[3m] Although considerable progress has been made in 1,4-enedione synthesis, the methods may suffer from availability of starting materials, low yield, or poor stereoselectivity. Thus, development of an efficient synthetic method from simple and general substrates is still required. In particular, highly stereoselective synthesis of (*Z*)-1,4-enediones remains a great challenge. In 2013, Wang et al. reported a two-step synthesis of (*Z*)-1,4-enediones, that is, initial synthesis of the *E*-isomers followed by white-light irradiation to achieve the *Z*-isomers via *E* → *Z* isomerization.[3a]

In the past decade, visible-light photocatalysis has attracted considerable attention due to environmental compatibility and versatility in promoting a large amount of synthetically important reactions.[4] In our previous research, we reported a radical cation [4 + 2] annulation of arylalkenes to give naphthalene derivatives, with an organic photosensitizer, 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes), under visible-light photocatalysis.[5] In the following work, we studied oxidative coupling of alkynes under photocatalytic conditions. Herein, we would like to communicate the oxidative dimerization of alkynes in the open air, leading to the production of (*Z*)-1,4-enediones in high efficiency and stereoselectivity. The photocatalytic and metal-free protocol with dioxygen in the air as the oxidant[6] represents a green and environmentally benign approach in the one-pot and direct conversion of alkyne substrates into (*Z*)-1,4-enediones.

Initially, we performed the oxidative dimerization reaction of phenylacetylene (**1a**) in the open air under various conditions (Table 1). With Acr^+-Mes (1 mol %) as the organic photocatalyst, only a trace amount of 1,4-enediones was observed (entry 1). This is rationalized by the fact that the oxidation potential of general alkynes (e.g., E_{ox} = +2.28 V vs SCE for phenylacetylene)[7] is higher than the excited reduction potential of Acr^+-Mes (E^*_{red} = +2.08 V vs SCE).[8] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) with a E^*_{red} = +3.18 V vs SCE was employed to oxidize phenylacetylene; however, no reaction occurred (entry 2). We assumed that dioxygen is probably incapable of achieving the catalytic cycle of DDQ.[9] 2,4,6-Triphenylpyrylium tetrafluoroborate (TPT, E^*_{red} = +2.28 V vs SCE)[10] is able to oxidize phenylacetylene, and the reaction in DCM gives rise to 1,4-enediones **2a** and **3a** in 52% yield with a *Z*/*E* ratio of 18:82 (entry 3).[11] The reaction conducted in DCE afford improved yield (75%) and *E*-isomer content (entry 4). Other solvents include THF, DMF, EtOH, and acetone proved to be inert. When EtOAc was selected as the solvent, a remarkably invertable *Z*/*E* ratio of 98:2 was observed, and the reaction time was shortened to 24 h (entry 5). Encouraged by the result, we introduced 4-(4-cyanophenyl)-2,6-diphenylpyrylium tetrafluoroborate (CN-TPT) with stronger oxidative ability to the reaction system. Satisfactory stereoselectivity was obtained (entry 6). However, the yield was fairly low (34%). This is probably due to the poor solubility of photosensitizer CN-TPT in EtOAc. To improve the solubility, DCE was tentatively added to the EtOAc system. A volume ratio of 10:1 between EtOAc and

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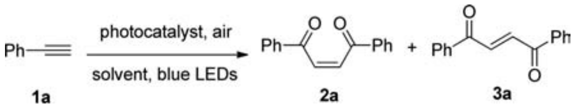
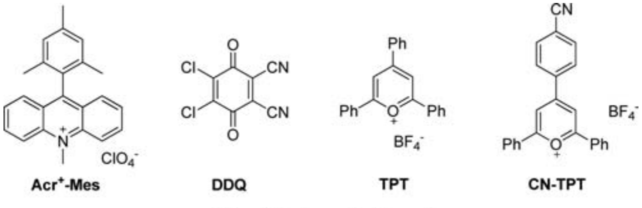
Table 1. Optimization of the Reaction Conditions[a]



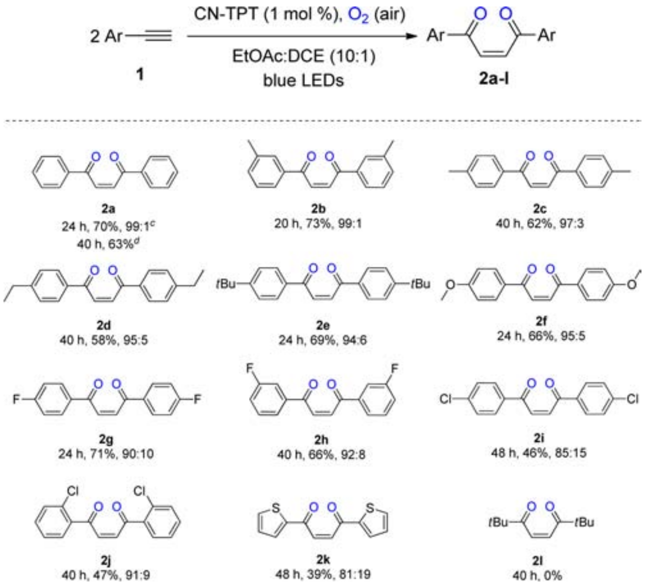
entry	photocatalyst	solvent	concentration (mol/L)	yield (%)[b]	Z/E (2a/3a)[c]
1[d]	Acr$^+$-Mes	DCM	0.25	trace	
2[d]	DDQ	DCM	0.25	nr	
3[d]	TPT	DCM	0.25	52	18:82
4	TPT	DCE	0.25	75	4:96
5	TPT	EtOAc	0.25	66	99:1
6	CN-TPT	EtOAc	0.25	34	98:2
7	**CN-TPT**	**EtOAc/DCE (10:1)**	**0.25**	**70**	**99:1**
8	CN-TPT	EtOAc/DCE (5:1)	0.25	69	90:10
9	CN-TPT	EtOAc/DCE (10:1)	0.1	60	92:8
10	CN-TPT	EtOAc/DCE (10:1)	0.5	44	98:2
11[e]	CN-TPT	EtOAc/DCE (10:1)	0.25	71	97:3
12[f]	CN-TPT	EtOAc/DCE (10:1)	0.25	nr	
13		EtOAc/DCE (10:1)	0.25	nr	
14[g]	CN-TPT	EtOAc/DCE (10:1)	0.25	62	95:5



photocatalysts used in this work

[a]Reactions were conducted with **1a** (0.5 mmol) and photocatalyst (1 mol %) in dry solvent at room temperature in the open air with 12 W blue LEDs for 24 h. [b]Isolated yield of **2a** and **3a**. [c]Ratio determined by ^{1}H NMR. [d]Reaction time was 40 h. [e]Catalyst loading: 5 mol %. [f]No light. [g]Under O_2 atmosphere; nr = no reaction.

Scheme 1. Synthesis of (*Z*)-1,4-Enediones from Terminal Alkynes via Homodimerization[a,b]



[a]Reactions were conducted with **1** (1 mmol) and photocatalyst (1 mol %) in dry solvents at room temperature in the open air with 12 W blue LEDs. [b]Isolated yield of **2**. [c]Ratio of *Z*/*E* determined by ^{1}H NMR. [d]Reaction was conducted with 5 mmol (0.51 g) **1a** and CN-TPT (1 mol %) in 5:1 EtOAc/DCE (20 mL) by sparging with air for 40 h.

DCE gave *Z*-isomer **2a** as the main product (70% yield, *Z*/*E* = 99:1) (entry 7). Further increase of the amount of DCE to 5:1 (volume ratio) relative to DCE led to undesired stereoselectivity (entry 8).[12] In addition, the solution concentration was examined. It was found that both higher and lower concentration (0.1 and 0.5 mol/L, respectively) led to decreased yields (entries 9 and 10). Increasing the catalyst amount to 5 mol % did not improve the reaction significantly (entry 11). Comparatively, in the absence of the photosensitizer or light, no target molecule was observed, validating the photocatalytic nature of this process (entries 12 and 13). Under an O_2 atmosphere, a decreased yield of **2a** and **3a** was observed, along with uncertain side products (entry 14).

Having established the optimal reaction conditions, we turned our attention to explore the substrate scope. As shown in Scheme 1, a variety of arylacetylenes could undergo oxidative homodimerization to give symmetric 1,4-diaryl-1,4-enediones with high *Z*-selectivity under standard conditions. Phenylacetylenes with electron-donating alkyls such as 3-methyl, 4-methyl, 4-ethyl, and 4-*tert*-butyl and alkoxyl group like 4-methoxyl on the phenyl ring gave the corresponding products **2b–f** in moderate to good yields. Reactions of halo-substituted phenylacetylenes containing 4-fluorine, 3-fluorine, 4-chlorine, and 2-chlorine also proceeded smoothly, providing products **2g–j** in 46–71% yields. Heteroaryl-substituted alkyne, 2-thienylacetylene, underwent the homocoupling reaction to afford (*Z*)-1,4-di(thiophen-2-yl)but-2-ene-1,4-dione (**2k**) in 39% yield. However, when aliphatic terminal alkynes such as *tert*-butylacetylene was subjected to the reaction sequence, the reaction was unsuccessful. This is consistent with the fact that aliphatic alkynes possess oxidation potential higher than that of aryl alkynes, which are more difficult to oxidize.[7] Note that the reaction of phenylacetylene was performed on a 5 mmol scale, affording (*Z*)-enedione **2a** in 63% isolated yield.

As asymmetric 1,4-enediones are important moieties in many pharmaceutical and natural molecules,[1] a protocol to achieve such products is of great value. We next shifted our focus to investigate the cross-coupling of two different alkynes. Initially, phenylacetylene containing electron-donating 4-*tert*-butyl, which is easier to be oxidized to the corresponding radical cation, due to the low oxidation potential, was chosen as the precursor. Excess amounts of arylacetylenes (2–3-fold) were introduced to the reaction system to capture the resulting radical cation intermediate corresponding to 4-*tert*-butylphenylacetylene.[13] As a result, a series of heterodimerized products **2m–p** were attained in 54–68% yields (Scheme 2). The substituents on the second aryl alkynes (**1′**) include hydrogen, 4-fluorine, 3-methyl, and 4-methyl. Similarly, reactions of 4-methoxyphenylacetylene with phenylacetylene (2 equiv), 4-methylphenylacetylene (2 equiv), 4-chlorophenylacetylene (3 equiv), and 2-thienylacetylene (3 equiv) proceeded well, giving the heterodimerized 1,4-enediones **2q–t** in 32–62% yields and good stereoselectivity. (*Z*)-1-Phenyl-4-(thiophen-2-yl)but-2-ene-1,4-dione (**2u**) was also prepared, albeit in low yield. Aliphatic *tert*-butylacetylene (3 equiv) was also chosen as the partner to couple with

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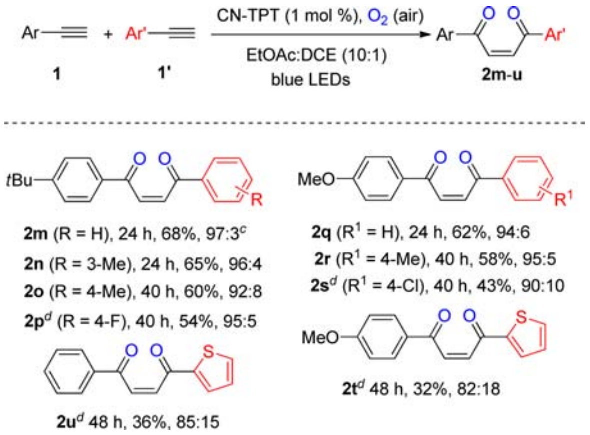
Scheme 2. Synthesis of (*Z*)-1,4-Enediones from Terminal Alkynes via Heterodimerization[a,b]

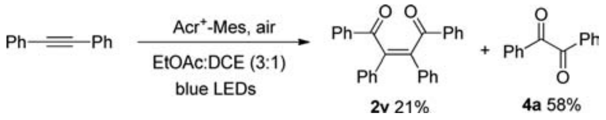


[a]Reactions were conducted with **1** (1 mmol), **1′** (2 mmol), and photocatalyst (1 mol %) in dry solvents at room temperature in the open air with 12 W blue LEDs. [b]Isolated yield of **2**. [c]Ratio of *Z*/*E* determined by ^{1}H NMR. [d]3 mmol of **1′** was added.

phenylacetylene, but only a trace amount of the cross-coupling product was observed according to the ^{1}H NMR of the crude mixture. The result is consistent with that reported by Mattes and Farid.[14a]

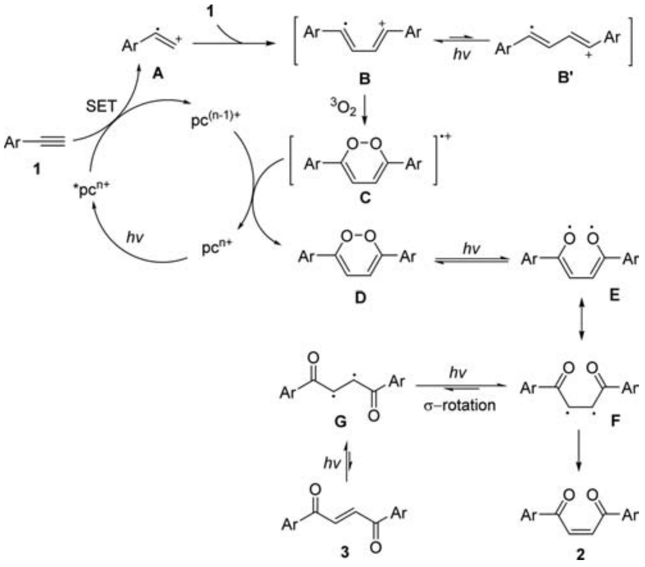
For internal alkynes like diphenylethyne, Acr$^+$-Mes (1 mol %) is a suitable organic photocatalyst. However, benzil **4a** was proven to be the main product (58% yield), and 1,4-enedione **2v** was produced in merely 21% yield (Scheme 3). This indicates that the reaction of the resulting radical cation with molecular oxygen occurs faster than the homodimerized coupling of the alkynes in this case.

Scheme 3. Investigation of the Reaction of Internal Alkynes



On the basis of all the results described above, a plausible mechanism for the formation of (*Z*)-1,4-enediones is proposed in Scheme 4. Under irradiation, pyrylium catalyst CN-TPT is excited to (CN-TPT)*, which oxidizes the alkyne **1**, generating a 1,2-radical cation **A** and the reduced pyran radical.[14] The electrophilic trap of intermediate **A** by a neutral alkyne molecule gives rise to a distal 1,4-radical cation **B**, which would further react with $^3O_2$ to produce 1,2-dioxin radical cation **C**.[14c] This electron-deficient species can oxidize the reduced pyran radical (to close the catalytic cycle), to give a neutral 1,2-dioxin **D**. Under visible-light irradiation, fragmentation via O−O homolytic cleavage in **D** gives *O*,*O*-1,6-diradical **E**, together with the resonance structure of *C*,*C*-1,2-diradical **F**. Rapid C−C double bond formation would deliver (*Z*)-1,4-enedione **2** as the final product. The highly stereoselective formation of (*Z*)-1,4-enediones **2** can be attributed to continuous visible-light illumination from blue LEDs (direct photochemical isomerization),[15] along with the possible energy transfer from excited photocatalyst CN-TPT to (*E*)-1,4-enedione **3** (for the absorption and emission spectra, see Figures S1−S4).[16] Thus, the possibility for formation of the *E*-isomers is inhibited to a large extent.

Scheme 4. Proposed Mechanism



In summary, we have developed a simple and direct method for (*Z*)-1,4-enedione synthesis by means of a photocatalytic oxidative homo- and heterodimerization of readily available arylalkynes. A mechanism of $C_{sp}-C_{sp}$ oxidative coupling/[4 + 2] cyclization (with triplet dioxygen)/fragmentive isomerization was proposed. Visible light plays a dual role in both sensitizing the organic photocatalyst CN-TPT and promoting the generation of the *Z*-isomer, which illustrates the highly stereoselective nature of this one-pot protocol. Oxygen in the open air is used as the terminal oxidant in the cascade process, making this organic photocatalytic system meet the requirements of green and eco-sustainable chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02926.

Experimental procedures and spectral data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: fsliang@lnu.edu.cn.

ORCID

Fushun Liang: 0000-0003-4195-3863

Notes

The authors declare no competing financial interest.

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(12) In the experiment, we found the formation of *E*-isomer as the main product in DCE (dark brown solution color) and predominant formation of *Z*-isomer in EtOAc (light yellow solution). The reason for the solvent effect is still unclear. It was assumed that light transmission plays a certain role in the stereoselective formation of 1,4-enediones.

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