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# Palladium-Catalyzed (3+3) Annulation of Allenylethylene Carbonates with Nitrile Oxides

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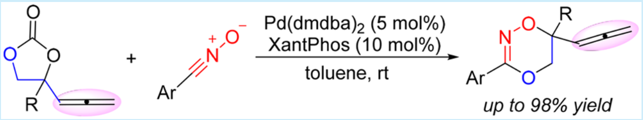
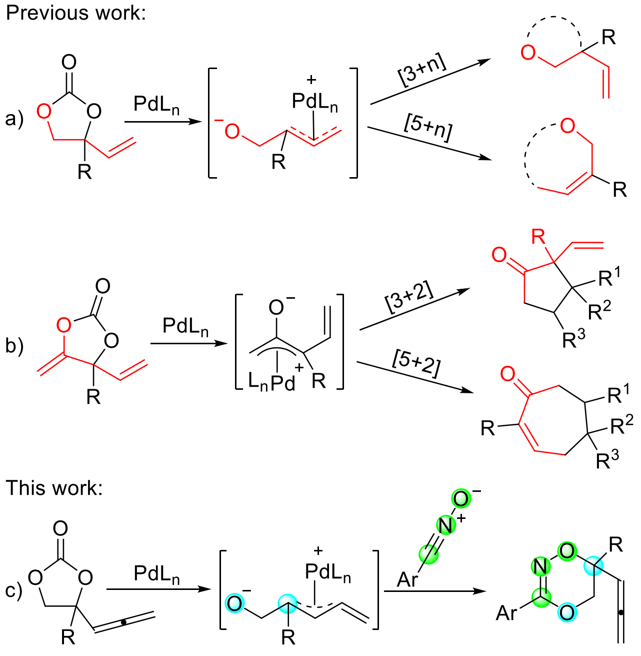
**ABSTRACT:** In this paper, we designed and synthesized a new type of cyclic carbonates, allenylethylene carbonates (AECs). With AECs as reactive precursors, we developed palladium-catalyzed (3+3) annulation of AECs with nitrile oxides. Various AECs worked well in this reaction under mild reaction conditions. A variety of 5,6-dihydro-1,4,2-dioxazine derivatives with allenyl quaternary stereocenters can be accessed in a facile manner in high yields (≤98%).



Allenes make up an important class of compounds that not only have versatile reactivities[1] but also are widespread in bioactive natural product and synthetic compounds, receiving special attention in bioactivity investigation.[2] Therefore, their synthesis has attracted a great deal of attention, and developing new synthetic methods for allene compounds is highly desirable.

Cyclic and acyclic carbonates have been extensively applied in palladium catalysis for cycloaddition and allylic substitution reactions through decarboxylative catalytic transformations.[3] Among those cyclic carbonates, vinylethylene carbonates (VECs) have been intensively studied in the past decade.[3k] Their reactivities have been well exploited, leading to the development of various (3+*n*)[4] and (5+*n*)[5] annulation reactions (Scheme 1a) and allylic substitution reactions. However, the potential of VECs in palladium catalysis has nearly been exhausted. In this context, some new variants of VECs have been reported. Most recently, the Zi group[6] and the Guo group[7] designed vinyl methylene cyclic carbonates (VMCCs) to act as reactive precursors to Pd-oxyallyl species independently for annulation reactions and developed [3+2] and [5+2] annulations of VMCCs with electron-deficient alkenes. Encouraged by our interest in the development of new Pd-catalyzed annulation reactions,[8] we considered the design of novel cyclic carbonates from different perspectives. Because of structural peculiarities, unique bonding properties, and versatile reactivities of allene compounds, we installed an allene motif onto cyclic carbonates and synthesized allenylethylene carbonates (AECs) (Scheme 1c). With AECs as reactive precursors for palladium catalysis, we herein present a Pd-catalyzed (3+3) annulation reaction of AECs with nitrile oxides, as shown in Scheme 1c.

**Scheme 1. Palladium-Catalyzed Decarboxylative Annulations**



Initially, we synthesized a series of AECs through two different synthetic procedures (Scheme 2; see the Supporting Information for details).[9] Various AECs were smoothly prepared. However, the yields were generally low in these syntheses. The conversion rate of every step was high, but allenyl cyclic carbonates could easily isomerize to propargyl

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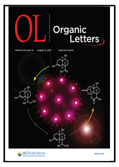

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**Scheme 2. Synthesis of Allenylethylene Carbonates (AECs)**

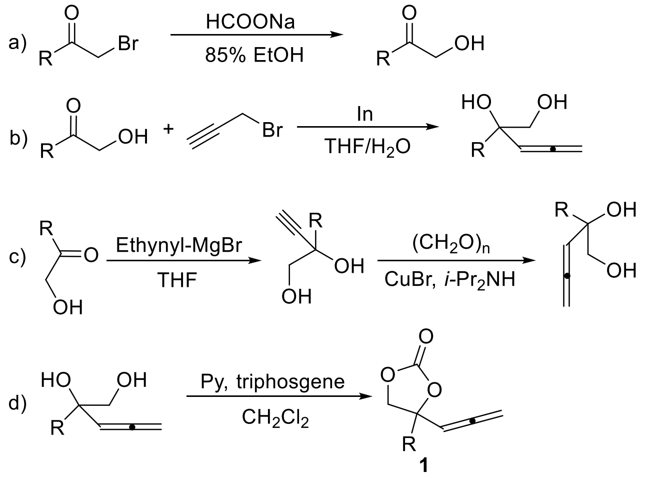
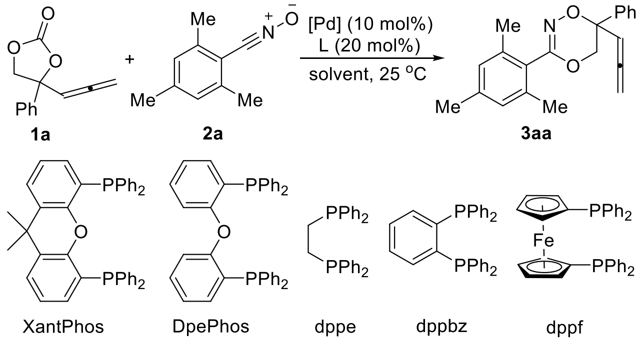


**Table 1. Optimization of Reaction Conditions for (3+3) Annulation of AEC 1a with Nitrile Oxide 2a**[a]



| entry | [Pd] | ligand | solvent | $t$ (h) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | none | none | $CH_2Cl_2$ | 48 | 0 |
| 2 | $Pd_2dba_3·CHCl_3$ | $PPh_3$ | $CH_2Cl_2$ | 48 | trace |
| 3 | $Pd_2dba_3·CHCl_3$ | XantPhos | $CH_2Cl_2$ | 16 | 78 |
| 4 | $Pd_2dba_3·CHCl_3$ | DpePhos | $CH_2Cl_2$ | 48 | 46 |
| 5 | $Pd_2dba_3·CHCl_3$ | dppe | $CH_2Cl_2$ | 48 | trace |
| 6 | $Pd_2dba_3·CHCl_3$ | dppbz | $CH_2Cl_2$ | 68 | 29 |
| 7 | $Pd_2dba_3·CHCl_3$ | dppf | $CH_2Cl_2$ | 68 | 26 |
| 8 | $Pd_2(dba)_3$ | XantPhos | $CH_2Cl_2$ | 13 | 87 |
| 9 | $Pd(dba)_2$ | XantPhos | $CH_2Cl_2$ | 24 | 82 |
| 10 | $Pd(PPh_3)_4$ | XantPhos | $CH_2Cl_2$ | 13 | 66 |
| 11 | $Pd(dmdba)_2$ | XantPhos | $CH_2Cl_2$ | 13 | 88 |
| 12 | $[Pd(\eta^3\text{-cinnamyl})Cl]_2$ | XantPhos | $CH_2Cl_2$ | 36 | 72 |
| 13 | $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ | XantPhos | $CH_2Cl_2$ | 28 | 13 |
| 14 | $Pd(dmdba)_2$ | XantPhos | DCE | 48 | 82 |
| 15 | $Pd(dmdba)_2$ | XantPhos | $CHCl_3$ | 48 | 92 |
| 16 | $Pd(dmdba)_2$ | XantPhos | toluene | 48 | 93 |
| 17 | $Pd(dmdba)_2$ | XantPhos | THF | 48 | 87 |
| 18 | $Pd(dmdba)_2$ | XantPhos | $PhCF_3$ | 48 | 91 |
| 19[c] | $Pd(dmdba)_2$ | XantPhos | toluene | 10 | 98 |
| 20[d] | $Pd(dmdba)_2$ | XantPhos | toluene | 10 | 90 |

[a] Unless noted otherwise, the reaction of **1a** (0.15 mmol), **2a** (0.1 mmol), [Pd] (10 mol %), and a ligand (20 mol % for $Ph_3P$, 10 mol % for diphosphines) was performed in 1 mL of solvent at 25 °C. Abbreviations: DCE, 1,2-dichloroethane; dba, dibenzylidene acetone; dmdba, 3,5,3′,5′-dimethoxydibenzylidene acetone. [b] Isolated yield. [c] With 5 mol % Pd $(dmdba)_2$ and 10 mol % XantPhos. [d] With 2.5 mol % Pd $(dmdba)_2$ and 5 mol % XantPhos.

cyclic carbonates in the separation step, leading to low isolated yields. With various AECs in hand, we then chose AEC **1a** and stable nitrile oxide **2a** as model reaction partners in dichloromethane at room temperature to investigate the optimal reaction conditions (Table 1). In the absence of a palladium catalyst and ligand, no (3+3) annulation product was observed (entry 1), indicating that the thermal [3+2] cycloaddition of allene with nitrile oxide did not occur. With $Pd_2dba_3·CHCl_3$ (5 mol %)/$PPh_3$ (20 mol %) as the catalyst, the trace amount of the product was observed (entry 2). Encouraged by this result, we next examined various phosphine ligands in the presence of $Pd_2dba_3·CHCl_3$. The use of XantPhos and Dpephos as ligands led to product **3aa** in 78% and 46% yields, respectively (entries 3 and 4, respectively). A common dppe ligand was almost ineffective in the reaction (entry 5). When dppbz and dppf were used, the reaction was sluggish, furnishing desired product **3aa** in 29% and 26% yields, respectively (entries 6 and 7, respectively). With the XantPhos as the ligand, we then evaluated several palladium catalysts (entries 8−13). Among them, $Pd(dmdba)_2$ displayed a good catalytic activity, resulting in the formation of the corresponding product in the highest 88% yield (entry 11). Interestingly, the use of $[Pd(\eta^3\text{-cinnamyl})Cl]_2$ in this reaction gave product **3aa** in 72% yield (entry 12), although $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ was less effective in providing **3aa** in 13% yield (entry 13). The solvent screening revealed that toluene is an appropriate solvent, and the yield of the desired product was increased to 93% (entries 14−18 and entry 17, respectively). In particular, when the catalyst loading was decreased to 5 mol %, the yield of desired product **3aa** was increased to 98% (entry 19). Further decreasing the catalyst loading to 2.5 mol % led to a little decrease in the yield (entry 20). On the basis of the results presented above, the optimal reaction conditions for the (3+3) annulation were ultimately identified as follows: $Pd(dmdba)_2$ (5 mol %) as a catalyst and XantPhos (10 mol %) as a ligand in toluene at room temperature.

Having established the optimal conditions, we tested a variety of AECs to explore the reaction scope. The results are summarized in Table 2. Generally, the reaction proceeded smoothly to give the corresponding products in high yields (entries 1−14). The substituted AECs having electron-withdrawing (F, Cl, and Br) and electron-donating (Me and OMe) groups on the phenyl ring of the AEC at the *para*, *meta*, or *ortho* position were well tolerated, producing a number of allenyl-substituted dioxazines (**3ba**−**3la**) in good to excellent yields (82−98%) (entries 1−12). The AEC with biphenyl moieties also performed the reaction well, leading to the formation of the corresponding product **3ma** in 71% yield (entry 13). In addition, this annulation reaction can be applied to the AEC substrate containing a 2-naphthyl group, and the corresponding product **3na** was obtained in 78% yield (entry 14). It is worth noting that methyl- and ethyl-substituted AECs displayed good reactivity, affording the corresponding product in 98% and 83% yields, respectively (entries 15 and 16, respectively). The cyclohexyl AEC was relatively sluggish, and its reaction required a higher catalyst loading (10 mol % Pd catalyst), giving the annulation product in 58% yield (entry 17). In particular, the installation of a heterocycle in the allenylethylene carbonate was also workable (entry 18).

We next investigated the scope of nitrile oxides **2**, as shown in Table 3. Stable nitrile oxide **2b** displayed good reactivity, and we performed (3+3) annulation with AEC **1a** to produce the corresponding product **3ab** in 81% yield (entry 1). The

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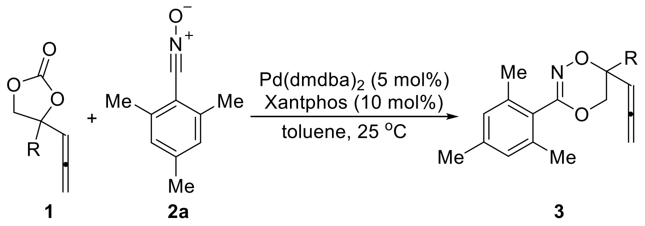
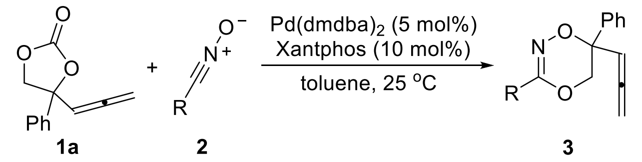
### Table 2. Scope of AECs for Pd-Catalyzed (3+3) Annulation[a]



| entry | R | *t* (h) | 3 | yield (%)[b] |
|---|---|---|---|---|
| 1 | Ph (**1a**) | 10 | **3aa** | 98 |
| 2 | 2-FC$_6$H$_4$ (**1b**) | 13 | **3ba** | 98 |
| 3 | 3-FC$_6$H$_4$ (**1c**) | 13 | **3ca** | 88 |
| 4 | 4-FC$_6$H$_4$ (**1d**) | 13 | **3da** | 90 |
| 5 | 3-ClC$_6$H$_4$ (**1e**) | 13 | **3ea** | 82 |
| 6 | 4-ClC$_6$H$_4$ (**1f**) | 12 | **3fa** | 98 |
| 7 | 3-BrC$_6$H$_4$ (**1g**) | 13 | **3ga** | 83 |
| 8 | 4-BrC$_6$H$_4$ (**1h**) | 12 | **3ha** | 94 |
| 9 | 4-MeC$_6$H$_4$ (**1i**) | 14 | **3ia** | 98 |
| 10 | 2-OMeC$_6$H$_4$ (**1j**) | 13 | **3ja** | 93 |
| 11 | 3-OMeC$_6$H$_4$ (**1k**) | 13 | **3ka** | 91 |
| 12 | 4-OMeC$_6$H$_4$ (**1l**) | 13 | **3la** | 98 |
| 13 | 4-PhC$_6$H$_4$ (**1m**) | 13 | **3ma** | 71 |
| 14 | 2-naphthyl (**1n**) | 14 | **3na** | 78 |
| 15 | Me (**1o**) | 5 | **3oa** | 98 |
| 16 | Et (**1p**) | 6 | **3pa** | 83 |
| 17[c] | cyclohexyl (**1q**) | 36 | **3qa** | 58 |
| 18 | 3-thienyl (**1r**) | 8 | **3ra** | 98 |

[a] Unless noted otherwise, the reaction mixture of **1** (0.15 mmol), **2a** (0.10 mmol), Pd(dmdba)$_2$ (5 mol %), and XantPhos (10 mol %) was stirred in 1 mL of toluene at 25 °C. [b] Isolated yield. [c] With 10 mol % Pd(dmdba)$_2$ and 20 mol % XantPhos.

### Table 3. Scope of Nitrile Oxides for Pd-Catalyzed (3+3) Annulation of AECs[a]



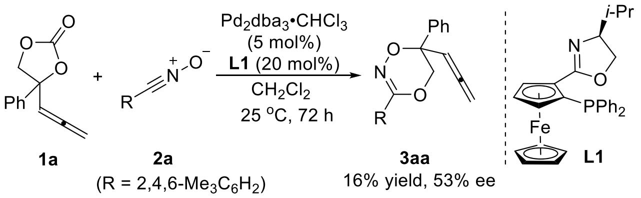
| entry | R | *t* (h) | 3 | yield (%)[d] |
|---|---|---|---|---|
| 1 | 2,6-Cl$_2$C$_6$H$_3$ (**2b**) | 5 | **3ab** | 81 |
| 2 | 2,6-Br$_2$C$_6$H$_3$ (**2c**) | 14 | **3ac** | 68 |
| 3[b] | 2,6-(OMe)$_2$C$_6$H$_3$ (**2d**) | 4 | **3ad** | 92 |
| 4 | 2,4,5-Me$_3$C$_6$H$_2$ (**2e**) | 17 | **3ae** | 67 |
| 5[c] | 4-MeC$_6$H$_4$ (**2f**) | 5 | **3af** | 41 |
| 6[c] | 2-naphthyl (**2g**) | 74 | **3ag** | 28 |

[a] Unless noted otherwise, the reaction mixture of **1a** (0.15 mmol), **2** (0.10 mmol), Pd(dmdba)$_2$ (5 mol %), and XantPhos (10 mol %) was stirred in 1 mL of toluene at 25 °C. [b] The reaction was performed at 40 °C. [c] The reaction mixture of the corresponding *N*-hydroxyformimimidol chloride (0.15 mmol), **1a** (0.1 mmol), NaOH (0.15 mmol), Pd(dmdba)$_2$ (5 mol %), and XantPhos (10 mol %) was stirred in 1 mL of toluene at 40 °C. [d] Isolated yield.

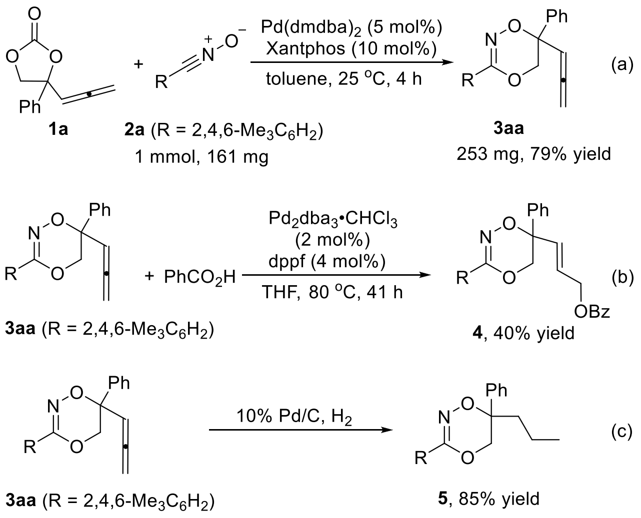
structure of product **3ab** was unambiguously confirmed by single-crystal X-ray diffraction analysis. In contrast, 2,6-Br$_2$-phenyl-substituted nitrile oxide **2c** has a relatively weak reactivity, resulting in the desired (3+3) annulation product **3ac** in 68% yield (entry 2). Nitrile oxide **2d** having a 2,6-OMe$_2$-phenyl group was reactive, affording desired product **3ad** in 92% yield (entry 3). When the reaction was carried out with 2,4,5-trimethyl-substituted nitrile oxide **2e**, the corresponding product **3ae** was formed in 67% yield (entry 4). Unstable nitrile oxides **2f** and **2g** generated in situ from the corresponding oxime halides in the presence of a base also worked in this reaction, providing the desired products **3af** and **3ag** in moderate 41% and 28% yields, respectively (entries 5 and 6, respectively). This indicated that oxime halides and the base in the reaction system seem to be unfavorable for the annulation.

Subsequently, the asymmetric variant of the current annulation reaction of AEC **1a** and nitrile oxide **2a** was investigated. Various chiral ligands were screened under the optimized reaction conditions. Unfortunately, we did not obtain satisfactory results in terms of enantioselectivity. In particular, in the presence of Pd$_2$dba$_3$·CHCl$_3$ (5 mol %) and ferrocene chiral phosphine ligand **L1** (20 mol %), cyclic product **3aa** was formed in 53% ee with a 16% yield (Scheme 3). The absolute configuration of chiral product **3aa** had not been assigned.

### Scheme 3. Asymmetric Variant of (3+3) Annulation



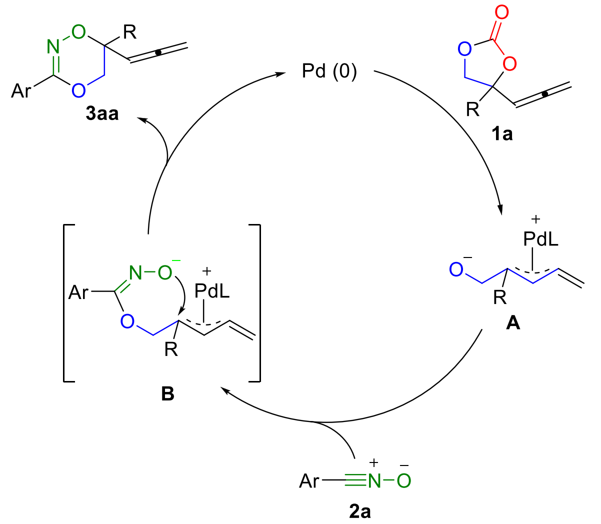
### Scheme 4. Scale-up Reaction and Transformation of the Product



As shown in Scheme 4, to demonstrate the efficiency and the extensibility of this catalytic process, a scale-up reaction of AEC **1a** and nitrile oxide **2a** was conducted under the optimized reaction conditions, furnishing annulation product **3aa** in 79% yield (253 mg). The potential synthetic utility of this protocol was then displayed through palladium-catalyzed hydrocarboxylation of product **3aa** with benzoic acid, giving the corresponding allyl ester **4** in 40% yield. In the presence of H$_2$ and 10% Pd/C, reduction product **5** was obtained in 85% yield.

A plausible mechanism is proposed as shown in Scheme 5. In the presence of a Pd catalyst, AEC **1** performs a ring-opening reaction to afford zwitterionic intermediate **A**, which attacks nitrile oxides **2** to give intermediate **B**. Subsequent intramolecular annulation led to a (3+3) annulation product **3**.

**Scheme 5. A Proposed Mechanism**



In conclusion, we have developed a palladium-catalyzed (3+3) annulation of AECs with nitrile oxides, offering a useful tool for the synthesis of 3,6-disubstituted 5-hydro-1,4,2-dioxazines. A broad range of AECs and nitrile oxides were compatible in this procedure, converting into the corresponding annulation compounds in moderate to excellent yields. A scale-up reaction and late-stage transformation of product **3aa** were also demonstrated. Further studies of the usability of the AECs in the synthesis of heterocyclic compounds for pesticide research are currently underway in our laboratory and will be reported in due course.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01921.

Experimental procedure, characterization data, NMR spectra, and X-ray crystallographic data (PDF)

### Accession Codes

CCDC 2065630 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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