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# Three-Bond Breaking of Cyclic Anhydrides: Easy Access to Polyfunctionalized Naphthalenes and Phenanthrenes

**Farnaz Jafarpour,* Hamideh Hazrati, and Sorour Nouraldinmousa**

*School of Chemistry, College of Science, University of Tehran, 14155-6455 Tehran, Iran*

*jafarpur@khayam.ut.ac.ir*

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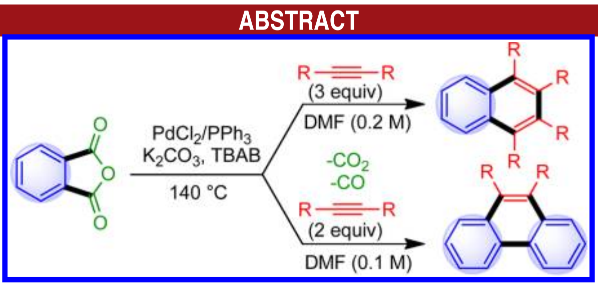
## ABSTRACT



**Benzannulation of phthalic anhydrides with alkynes to polyfunctionalized naphthalenes and phenanthrenes was confirmed to be straightforward using a palladium catalytic system. Sequential liberation of CO$_2$ and CO occurred via oxidative decomposition of anhydride. In the case of 1,8-naphthalenedicarboxylic anhydrides, both aryls were encompassed in the annulation reaction to afford acenaphthylenes.**

Polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and phenanthrene derivatives are an important class of materials because of their application in material science, nanotubes, light emitters, semiconductors, light-absorption dyes, and liquid crystals.[1] In addition, polyfunctionalized PAHs have attracted much attention because of their solubility, stability, and enhanced charge transfer and fluorescence properties.[2] Accordingly, the chemists continue to devise new synthetic methods to efficiently construct these structural motifs. Among various synthetic routes to $\pi$-conjugated naphthalenes,[3]

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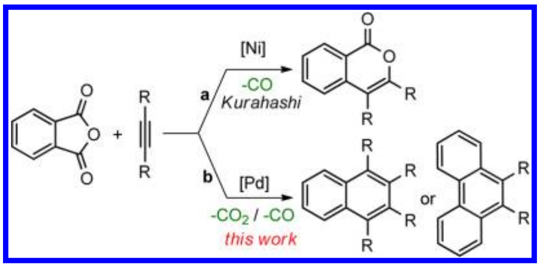
homologation of mono-[4] or difunctionalized[5] arenes have attracted much attention. Cyclotrimerization of arynes, benzannulation of biaryls, and cyclization of certain diarylethenes are developed synthetic strategies to phenanthrenes as well.[6] Limited functional group compatibility, low regioselectivity, and harsh reaction conditions for the in situ generation of arynes and the requisite use of prefunctionalized precursors are some drawbacks of the stated methods.

On the other hand, carboxylic anhydrides as cheap, safe, and widely accessible starting materials are precious components in metal-catalyzed cross-coupling reactions. Insertion of low-valent late transition metals into the carbonyl–oxygen bond and further CO liberation should be one of the most useful transformations for the regioselective construction of C–C bonds.[7]

Despite the high potential, anhydrides have rarely been added to the substrate scope of palladium-catalyzed decarbonylative transformations.[8] Furthermore, there is no precedent for consecutive decarboxylative– decarbonylative cross-coupling of cyclic anhydrides via a palladium-benzyne intermediate. Recently, Kurahashi reported a nickel-catalyzed decarbonylative cycloaddition of phthalic anhydrides with alkynes to form isocoumarins (Scheme 1, path a).[9] They also developed the reaction to allenes to construct $\delta$-lactones.[10] We now report our new findings that sterically hindered polycyclic aromatic hydrocarbons such as naphthalenes and phenanthrenes can be produced via consecutive decarboxylative–decarbonylative cross-coupling of phthalic anhydrides followed by alkyne insertion using palladium in place of nickel (Scheme 1, path b).

**Scheme 1.** Coupling of Phthalic Anhydrides with Alkynes



This protocol features attractive synthetic aspects such as employment of inexpensive anhydrides, mild reaction conditions, and various functional group tolerances. Furthermore, it is an unprecedented construction of a Pd–benzyne intermediate from a cyclic anhydride as most disubstituted benzyne precursors are unsymmetrical.[11] Extrusion of both CO$_2$ and CO molecules under mild reaction conditions and lower temperatures[12] provides a straightforward and experimentally simple new route to either phenanthrene or naphthalene derivatives from phthalic anhydrides, depending on the reaction stoichiometry as well as acenaphthylene derivatives in the case of naphthalenedicarboxylic anhydride. Furthermore, this protocol opens the opportunity for the waste-minimized construction of PAHs with only volatile side products.

To begin we attempted the addition of anhydride **1a** to diphenylacetylene **2a** applying reaction conditions in a similar way to the pioneering work of Stephan and de Vries for the decarbonylative Heck reaction of acid anhydrides (Table 1, entry 1):[8o] However this resulted in the formation of only traces of the desired naphthalene **3a**. Further optimization showed that addition of a phosphine ligand and 2 equiv of Ag$_2$CO$_3$ slightly improved the yield (entry 2). Among the various palladium sources examined, PdCl$_2$ showed superior catalytic reactivity (entries 2–4). The catalytic efficiency was further improved when

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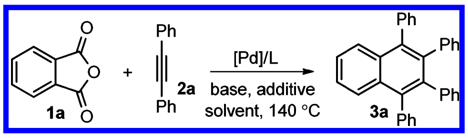
$Ag_2CO_3$ was replaced with $K_2CO_3$ (entry 5). Screening reactions with respect to additives and solvents proved TBAB and DMF as the most effective ones, respectively (entries 6–12). A slow dropwise addition of alkyne also proved to be effective in reducing the alkyne polymerization side reaction and improving the yield of phthalic anhydride benzannulation (entry 10). The control experiment in the absence of the catalyst resulted in the recovery of starting materials (see Supporting Information). Using $PdCl_2$ (10 mol %), $K_2CO_3$ (2.0 equiv), and TBAB (20 mol %) in DMF at 140 °C for 2 h led to the formation of the highly substituted naphthalene **3a** in 78% yield.

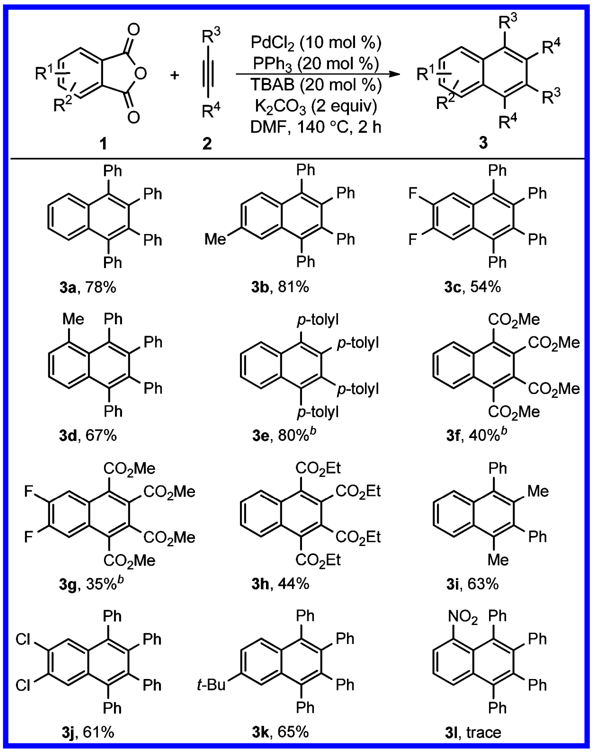
**Table 1.** Optimization of Catalyzed Benzannulation Reaction[a]



| entry | [Pd] | base | add. | solv. | yield (%)[b] |
|---|---|---|---|---|---|
| 1[c] | $PdCl_2$ | — | NaBr | NMP | 11 |
| 2 | $PdCl_2$ | $Ag_2CO_3$ | NaBr | NMP | 28 |
| 3 | $Pd(OAc)_2$ | $Ag_2CO_3$ | NaBr | NMP | 20 |
| 4 | $Pd(acac)_2$ | $Ag_2CO_3$ | NaBr | NMP | 10 |
| 5 | $PdCl_2$ | $K_2CO_3$ | NaBr | NMP | 47 |
| 6 | $PdCl_2$ | $K_2CO_3$ | $ZnCl_2$ | NMP | 37 |
| 7 | $PdCl_2$ | $K_2CO_3$ | LiOAc | NMP | 30 |
| 8 | $PdCl_2$ | $K_2CO_3$ | TBAB | NMP | 50 |
| 9 | $PdCl_2$ | $K_2CO_3$ | TBAB | toluene | 62 |
| **10** | **$PdCl_2$** | **$K_2CO_3$** | **TBAB** | **DMF** | **70 (78)**[d] |
| 11 | $PdCl_2$ | $K_2CO_3$ | TBAB | DMSO | 55 |
| 12 | $PdCl_2$ | $K_2CO_3$ | TBAB | Dioxane | 10 |

[a] Reaction conditions: Phthalic anhydride (0.1 mmol, 1 equiv), diphenylacetylene (3 equiv), palladium catalyst (10 mol %), $PPh_3$ (20 mol %), base (2 equiv), additive (20 mol %), solvent (0.2 M), 140 °C, 24 h. [b] Isolated yields. [c] Ligand-free. [d] The reaction was conducted for 2 h. Yield in parentheses refers to a 2 h slow dropwise addition of alkyne.

**Scheme 2.** Palladium Catalyzed Benzannulation of Phthalic Anhydrides with Alkynes to Construct Naphthalenes[a]



[a] Optimized conditions. [b] Reaction conditions: $Pd(OAc)_2$ (10 mol %), $PPh_3$ (20 mol %), $Ag_2CO_3$ (2 equiv) in NMP (0.2 M) at 160 °C for 24 h.

Having thus found the optimized reaction condition for the construction of tetraphenyl substituted naphthalene, we next investigated the effect of electronic and structural variations of both substrates. Scheme 2 outlines the scope of the benzannulation reaction where both electron-rich and -deficient phthalic anhydrides were well tolerated. Phthalic anhydrides containing methyl groups afforded the desired naphthalenes **3b** and **3d** in 67–81% yields.

The dihalogenated anhydride **1c** also survived the reaction conditions and afforded **3c** as a good partner for further functionalization in moderate yield. 1,2-Di-*p*-tolylethyne **2b** was employed next, and an up to 80% yield of the desired naphthalene **3e** was gratefully obtained.

Alkynes with electron-withdrawing methyl- and ethylester groups **2c** and **2d** also resulted in tetraalkyl ester substituted naphthalenes **3f**, **3g**, and **3h** albeit in lower yields. This would provide multiple points for further synthetic diversification. Employing an asymmetric aryl alkyl acetylene **2e** pleasingly resulted in only one of the three possible regioisomeric products **3i** with a 63% yield. Notably, an anhydride bearing two chloride substituents went through benzannulation and afforded **3j** with intact halo groups providing an opportunity for the construction of highly functionalized naphthalenes. A sterically hindered anhydride bearing a *tert*-butyl group also tolerated the reaction conditions to afford naphthalene **3k** in 65% yield. Finally, our attempts to extend the scope of the reaction to the phthalic anhydride bearing a nitro group was not successful and only a trace of the desired naphthalene **3l** was obtained. A nonaromatic precursor such as maleic anhydride and dialkyl acetylenes proved to be ineffective in this annulation reaction.

Intriguingly, we found that naphthalenedicarboxylic anhydride **4** participated in a selective benzannulation reaction with diphenylacetylene to provide 1,2-diphenylacenaphthylene **5a** in excellent yield (Scheme 3). The annulation reactions also proceeded smoothly with dialkyl acetylene derivatives leading to the construction of dialkyl acenaphthylenes **5b** and **5c** in satisfactory yields. These cyclopentene-fused polycyclic aromatic hydrocarbons are useful intermediates in the construction of curve-shaped PAHs.[13]

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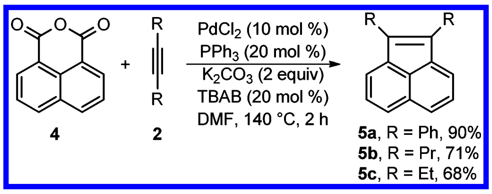
**Scheme 3.** Annulation Reactions of Diphenylacenaphthylene

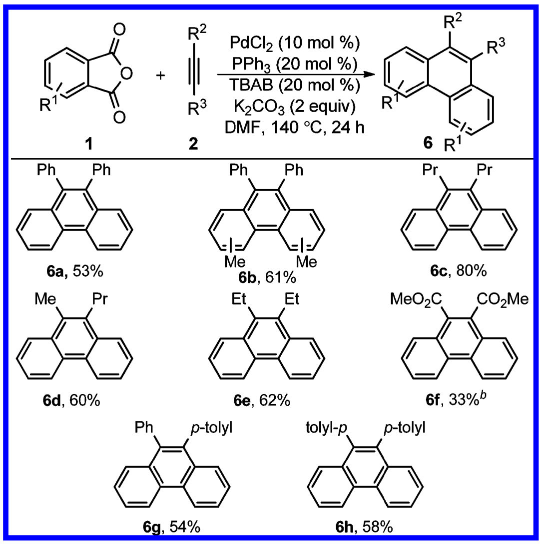


During the course of these studies, we discovered that with slightly altered reaction conditions, phenanthrenes were constructed (Scheme 4). Benzannulation of anhydride **1a** with a reduced amount of alkyne **2a** and increased amount of solvent led to 9,10-diphenyl phenanthrene **6a** in 53% yield. With methyl substituted anhydride, a mixture of the regioisomeric products **6b** were obtained with no selectivity. We were pleased to see that dialkyl acetylene derivatives which usually display lower reactivity compared to diaryl acetylenes[14] were also tolerated under the reaction conditions and selectively afforded 9,10-dialkyl substituted phenanthrenes **6c**–**6e** in yields exceeding 60%. Reduced amounts of DMAD also resulted in the corresponding phenanthrene albeit in a lower yield. *p*-Tolyl-substituted alkynes also afforded PAHs **6g** and **6h** in good yields.

A plausible mechanism for the benzannulation reaction of anhydrides is proposed in Scheme 5. Oxidative addition of palladium to the carbonyl–oxygen bond leads to the formation of acylpalladium carboxylate metallacycle **A** as the key intermediate. Next, to discriminate between two competitive paths of CO$_2$ or CO extrusion, indenone **7** was isolated in the course of the reaction (path a). The evidence suggests that CO$_2$ extrusion followed by alkyne insertion precedes CO extrusion. Finally, CO liberation followed by the insertion of the second alkyne molecule leads to naphthalene **3** (path **b**). On the other hand, our preliminary investigation revealed that despite the participation of 1,8-naphthalic anhydride in this reaction, the possibility of intermediate formation of an aryne with cyclic anhydrides could not be definitely ruled out. An aryne trimerization of anhydride **1b** proceeded in the absence of an alkyne coupling partner to afford triphenylene **8** in 31% isolated yield.

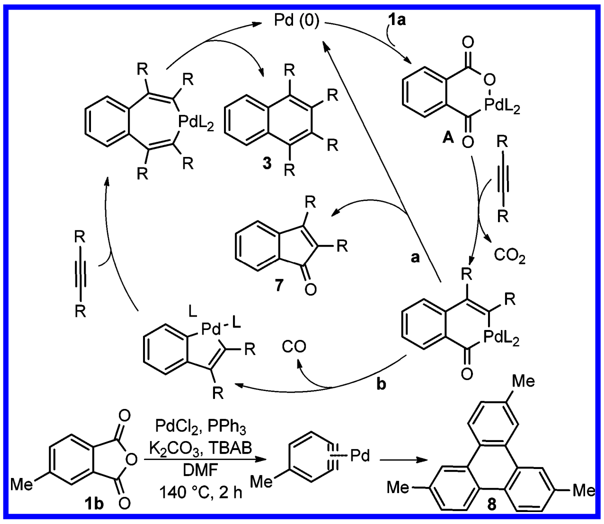
In conclusion, we have developed a new method for decarboxylative and decarbonylative addition of cyclic anhydrides to alkynes. The protocol allows for the waste-minimized construction of sterically congested naphthalenes and phenanthrenes employing a palladium catalyst. The practical construction of disubstituted acenaphthylenes is also realized using 1,8-naphthalenedicarboxylic anhydride. The reaction shows generality and good functional group tolerance. Further efforts to expand the scope of the reaction are ongoing.

**Scheme 4.** Palladium Catalyzed Benzannulation of Phthalic Anhydrides with Alkynes To Construct Phenanthrenes[a]



[a] Reaction conditions: Anhydride (0.1 mmol), alkyne (2 equiv), PdCl$_2$ (10 mol %), PPh$_3$ (20 mol %), K$_2$CO$_3$ (2 equiv), TBAB (20 mol %), DMF (0.1 M), 140 °C for 24 h. [b] Reaction conditions: Pd(OAc)$_2$ (10 mol %), PPh$_3$ (20 mol %), Ag$_2$CO$_3$ (2 equiv), NMP (0.1 M), 160 °C for 24 h.

**Scheme 5.** Plausible Mechanism



**Supporting Information Available.** Detailed experimental procedures and spectroscopic data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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