Palladium-Catalyzed Trimerizations of Terminal Arylalkynes: Synthesis of 1,3-Diaryl-2-arylethynyl-1,3-butadienes

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Alkynes contain one or more carbon - carbon triple bonds and belong to the class of unsaturated hydrocarbons. They are important building blocks in common organic molecules, natural products and organic conducting materials. The dual $\alpha$ and $\pi$ nature of terminal acetylenes can be easily activated by metal catalysts and allows for various reaction types, particularly for C - C bond formation. Recently, we observed that a new trimerization adduct 2 could be synthesized directly from alkynes 1 (Scheme 1). To the best of our knowledge, this is the first example for the generation of a dienyne with this skeleton by the trimerization of a terminal alkyne. Herein, we optimized reaction conditions and studied their regioselectivity, scope and limitations. Systematic studies of the reaction conditions revealed that palladium catalyst, base, solvent and temperature all play key roles. Upon heating phenylacetylene 1 (Ar = Ph) in acetonitrile with a mixture of PdCl$_2$(PPh$_3$)$_2$, PPh$_3$, NEt$_3$ and CuI, angular dienyne 2 (Ar = Ph) can be synthesized with high regioselectivity in 94% yield.

The reactivity of several alkynes has been examined in this reaction (Scheme 1). Most arylalkynes produced the corresponding dienynes 2 in good yields with ($Z$)-regioselectivity. In some examples, the electronic and steric properties of the aryl substituent in an alkyne 1 affected the yield and the regioselectivity. Angular trimerization of an alkyne with a sterically congestive substituent caused the formation of a significant amount of enynes 3. Two derivatives of ($Z$)-2 were crystallized from CHCl$_3$/MeOH and their structures were confirmed by the X-ray analyses (Figure 1).
Enynes 3 were assumed as the intermediates in this reaction. Addition of an alkyne 1 to aryl-substituted enynes 3 in the same reaction conditions, indeed, yielded dienynes 2 (Scheme 2). In comparison to the trimerization of terminal alkynes 1, dienynes 2 generated through the hydroalkynylation of enynes 3 did not give satisfactory results, which arise from the instability of 1,3-diaryl-3-buten-1-yne 3 (R1 = R2 = Ar). It has also been observed that alkynes 1 and enynes 3 affected the stereochemistry of dienynes 2.

In conclusion, we provide a new and simple procedure for generating trimerization adducts 2 from terminal arylalkynes 1 in one pot. This protocol indicates that enynes 3 are much more reactive than alkynes 1 towards hydroalkynylation to yield dienynes (Z)-2. Elaboration of this methodology and investigation of other catalytic applications in the construction of complex aromatic molecules and polymers are in progress.