Synthesis and Reactivity of a Terminal 1-Alkynyl Triazene

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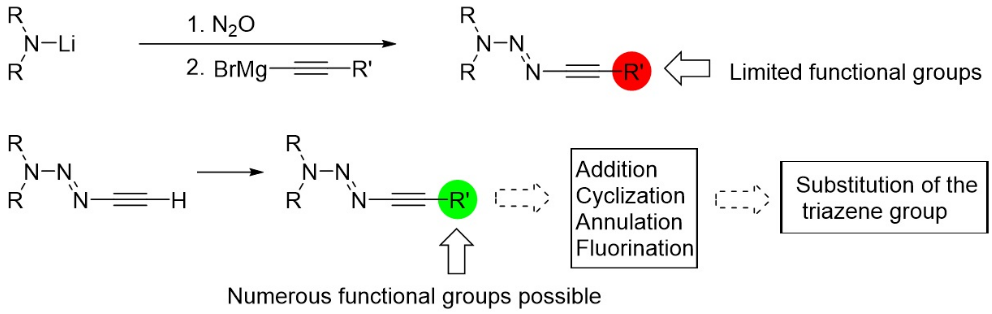
1-Alkynyl triazenes have emerged as highly versatile reagents in organic synthesis.[1] The electron-donating character of the triazene group activates the triple bond, resulting in ynamide-like reactivity. 1-Alkynyl triazenes can be employed as suitable substrates for a variety of reactions, including cycloadditions, annulations, rearrangements, and 1,2-additions, as well as fluorination reactions. A distinct advantage of using 1-alkynyl triazenes in these transformations is the possibility for further derivatizations of the products. Under acidic conditions, the triazene function can be substituted by a variety of nucleophiles, facilitating divergent product modifications.[1]

Thus far, 1-alkynyl triazenes have been accessible only by one synthetic route, namely, the coupling of lithium amides with first nitrous oxide (N_2O) and then an alkynyl Grignard reagent.[2] The utilization of strongly basic and nucleophilic reagents severely restricts the functional groups, which can be employed. We have now developed a procedure for the synthesis of a terminal 1-alkynyl triazene.[3] The easy-to-access compound enables the preparation of 1-alkynyl triazenes with a range of functional groups including esters, alcohols, cyanides, phosphonates, and amides. The availability of functionalized 1-alkynyl triazenes makes this class of compounds attractive for applications in organic synthesis. The terminal 1-alkynyl triazene can also be used for the synthesis of di- and triynes and for the preparation of (hetero)aromatic triazenes via transition-metal-catalyzed cyclization reactions.[3]



Scheme 1. Versatile reactivity of terminal 1-alkynyl triazene

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[2] G. Kiefer, T. Riedel, P. J. Dyson,R. Scopelliti, K. Severin, *Angew. Chem., Int. Ed.* **2015**, 54, 302−305.
[3] C. T. Bormann, C. Mathew, M. M. António, A. T. F. Fadaei-Tirani, Kay Severin, *J. Org. Chem.* **2022**, 24, 16882–16886.