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N-Alkynylpyridinium Salts: Highly Electrophilic Alkyne–Pyridine Conjugates as Precursors of Cationic Nitrogen-Embedded Polycyclic Aromatic Hydrocarbons

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## All Kinds of Alkynylpyridiniums: Elusive Salts Now Plentiful

**Significance:** *N*-Alkynylpyridinium salts (e.g., 1) have eluded isolation in previous attempts to synthesize these electrophilic molecules. Herein, the researchers disclose that alkynyl iodanes 2 are highly effective reagents for the preparation of a wide range of *N*-alkynylpyridinium triflates directly from pyridines. This method enabled the first full characterization of an *N*-alkynylpyridinium salt and the exploration of further transformations, including the synthesis of 'nitrogen-doped' polycyclic aromatic compounds with promising electronic properties for materials applications.

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**Comment:** Excellent yields are reported for the alkynylation of variously substituted pyridines as well as other aza-heterocycles. The *N*-alkylpyridinium triflates are stable under ambient conditions for at least six months, but the alkyne unit can be transformed in dipolar cycloaddition, halogenation, and hydrofunctionalization reactions. Halogenated products bearing a 2-aryl substituent were further subjected to photocyclization—dehydrohalogenation to generate quinolizinium salts (e.g., 3 and 4), and fluorescent compounds such as 6 were formed directly in the alkynylation of 2-imidazolylpyridines 5.

Category

Synthesis of Materials and Unnatural Products

Key words

pyridinium
hypervalent iodine
photocyclization

