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.

**Comment:** Excellent yields are reported for the alkynylation of variously substituted pyridines as well as other aza-heterocycles. The \(N\)-alkynylpyridinium 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 quinolizinum salts (e.g., 3 and 4), and fluorescent compounds such as 6 were formed directly in the alkynylation of 2-imidazolylpyridines 5.

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