**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 iodonanes 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 alkylation 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 quinolizinium salts (e.g., 3 and 4), and fluorescent compounds such as 6 were formed directly in the alkylation of 2-imidazolylpyridines 5.

**KEY WORDS**
- pyridinium
- hypervalent iodine
- photocyclization