Synthesis and Applications of Diaryliodonium Salts

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Diaryliodonium salts have recently gained considerable attention as environmentally benign, reactive and selective electrophilic arylation reagents with a variety of nucleophiles. The lack of efficient synthetic routes towards diaryliodonium salts has previously limited their scope as reagents in organic chemistry. We have recently developed several one-pot syntheses of diaryliodonium triflates, tosylates and tetrafluoroborates. These complimentary routes provide access to a wide range of both symmetric and unsymmetric salts with various functional groups.

These electrophilic arylation agents have been applied in arylation of various oxygen nucleophiles under mild and metal-free conditions, providing facile routes to diaryl ethers, alkyl aryl ethers, aryl esters and aryl sulfonates. Chemoselectivity aspects, mechanistic studies and an unexpected, nucleophile-assisted ligand exchange will also be discussed.

Arylation of alcohols:

\[ \text{Ar}_1^+ \text{I} \text{Ar}_2^- + \text{R}-\text{OH} \xrightarrow{\text{NaOH, H}_2\text{O}} \text{R}^-\text{O}^-\text{Ar}_1 \]

allylic alcohols up to 79%
benzylic alcohols up to 92%
phenols up to 98%

Chemoselectivity studies:

\[ \text{Nu}^- + \text{Ar}_1^+ \text{I} \text{Ar}_2^- \xrightarrow{\text{rt or 50 }^\circ\text{C}} \text{Nu}^-\text{Ar}_1^- + \text{Ar}_2^-\text{I} \]

Aryl exchange:

\[ \text{Ar}_1^+ \text{X}^- \xrightarrow{\text{rt}} \text{Ar}_2^+ \text{X}^- + \text{Ar}_1^-\text{X}^- \]