

# SYNLETT Spotlight 381

## Diaryliodonium(III) Salts: Arylating Agents

Compiled by Nobutaka Yamaoka



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Nobutaka Yamaoka was born in Gifu, Japan. He received his M.Sc. (2011) in chemistry from Ritsumeikan University. Currently, he is working toward his D.Sc. degree under the supervision of Professor Yasuyuki Kita. His research interests focus on metal-free oxidative bond formation utilizing hypervalent iodine compounds.

College of Pharmaceutical Sciences, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan  
E-mail: rc011058@ed.ritsumeai.ac.jp

### Introduction

Diaryliodonium(III) salts,  $\text{ArI}^+\text{Ar}'\text{X}^-$  ( $\text{Ar}$ ,  $\text{Ar}' = \text{aryl}$ ), are classically known as trivalent iodine species with two aryl ligands bound to an iodine atom. These are readily available and easy-to-handle compounds, and typically form stable crystals. The salts tend to convert into more stable monovalent iodoarenes under reductive conditions. Due to the good leaving ability of the iodoarene groups, they are used as arylating reagents in various reactions, for example, nucleophilic substitution reactions with various nucleophiles, such as organometallic agents, enolates,<sup>1</sup> and heteroatom nucleophiles,<sup>2</sup> and coupling reactions using transition-metal catalysts.<sup>3</sup> They are also valuable as benzyne precursors.<sup>4</sup> Recently, a number of new C–H

bond arylations for providing biaryls have been reported.<sup>5</sup> In specific cases, they serve as unique arylating agents under metal-free conditions.<sup>6</sup>

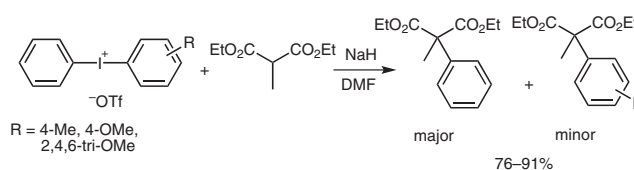
### Preparation

Some diaryliodonium(III) salts are commercially available. Non-commercial salts can be prepared from organometallic compounds by condensation with hypervalent iodine reagents,<sup>7</sup> or arenes themselves under heating and/or strong acidic conditions.<sup>8</sup> Recently, versatile direct approaches have been achieved for preparing diaryliodonium(III) salts.<sup>9</sup> They can be typically isolated as fine powders by trituration with ether.

### Abstracts

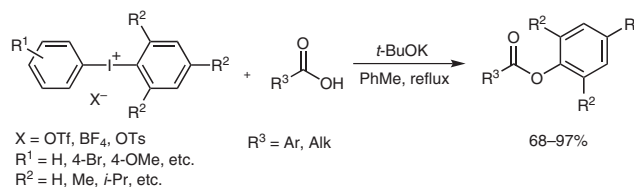
#### (A) Nucleophilic Substitution Reaction:

Alkyl-substituted malonates and  $\alpha$ -keto esters could be efficiently arylated by diaryliodonium salts in the presence of base to give the corresponding aryl derivatives under mild conditions.<sup>1b</sup> The electron-rich aromatic ring was less reactive, and thus the electron-deficient aromatic ring selectively reacted in this reaction.



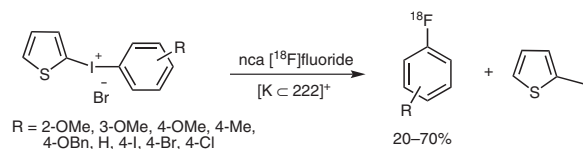
#### (B) Arylation of Carboxylic Acids:

An efficient arylation of carboxylic acids with diaryliodonium salts was developed, giving aryl esters in high yields within short reaction times.<sup>2d</sup> The transition-metal-free conditions were compatible with a range of functional groups, and a good chemoselectivity was observed with the unsymmetric diaryliodonium salt according to the interplay of the steric demand, ortho effect, and/or the electron deficiency of the aromatic rings.



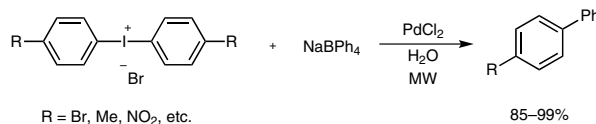
#### (C) Selective Fluorination Utilizing Heteroaromatic Iodonium Salts:

Diaryliodonium salts containing the  $\alpha$ -thienyl group as an electron-rich heteroaromatic moiety proved to be potent precursors for the nucleophilic, regioselective no-carrier-added (nca) radiofluorination of various arenes.<sup>2f</sup> The fluorination of the thiophene ring would not occur at all, and the nucleophilic introduction of nca [<sup>18</sup>F]fluoride into electron-rich aromatic compounds was possible in one step.



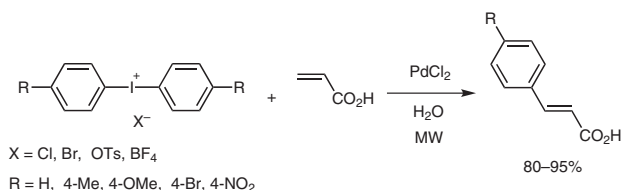
## (D) Suzuki Coupling with Sodium Tetraphenylborate:

The palladium chloride catalyzed Suzuki coupling reaction of sodium tetraphenylborate with diaryliodonium salts was achieved by microwave irradiation in water without using base.<sup>3a</sup> This convenient method for the rapid formation of aryl carbon–carbon bonds occurred in excellent yields.



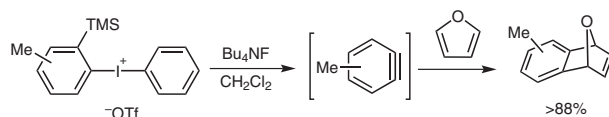
## (E) Use in Heck Reaction:

A fast and convenient base-free Heck reaction of acrylic acids and allyl alcohols with diaryliodonium salts was achieved in water by microwave irradiation, providing a simple method for the synthesis of *trans*-cinnamic acids and cinnamyl alcohols in good yields in a short reaction time.<sup>3b</sup>



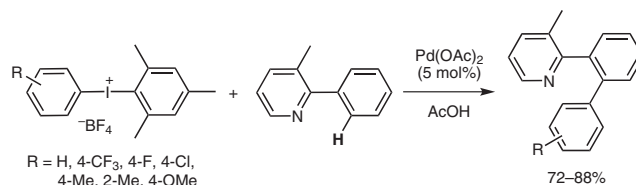
## (F) Use as Benzyne Precursors:

The treatment of (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflates with tetrabutylammonium fluoride could be utilized for the high yields of benzyne adducts in the presence of a trapping agent such as furans.<sup>4</sup> Especially, the high-yield reactions would indicate the quantitative generation of benzynes and their efficient capture by the furans.



## (G) Oxidative C–H Activation/C–C Bond Formation:

A new palladium-catalyzed method involving C–H activation/C–C bond formation using diaryliodonium salts as arylating agents was recently reported.<sup>5a</sup> This transformation has been applied to a variety of arenes and benzylic substrates having different directing groups (pyridines, quinolines, oxazolidinones, and amides), and could proceed with high levels of regiocontrol.



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