

## Chemoselectivity Investigation in Arylations with Diaryliodonium Salts

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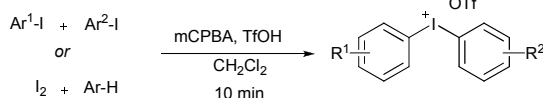
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### INTRODUCTION

Arylations are important transformations in organic synthesis. Aryl ethers, aryl esters and  $\alpha$ -aryl carbonyl compounds are important substructures in a variety of compounds such as pharmaceuticals and natural products.<sup>1</sup>

Diaryliodonium salts have recently been recognized as versatile reagents in organic synthesis.<sup>2</sup> They can be employed both in metal-mediated and metal-free reactions, thereby avoiding the drawbacks of organometallic reagents *i.e.* toxicity and high cost.<sup>3</sup> Efficient one-pot procedures to diaryliodonium salts have been developed within our group (Scheme 1) increasing the availability of these compounds.<sup>4</sup>

**Scheme 1.** One-pot routes to diaryliodonium salts

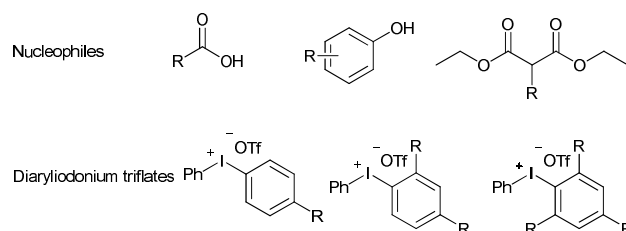


With fast and inexpensive procedures for the preparation of these salts in hand, we are currently investigating the electrophilic arylating potential of these reagents.<sup>5</sup>

### RESULTS AND DISCUSSION

Unsymmetric diaryliodonium salts ( $\text{R}^1 \neq \text{R}^2$ ) are sometimes preferred due to economic and accessibility reasons. Thus it is important to understand and predict which aryl moiety is transferred to the nucleophile, *i.e.* the chemoselectivity of the process. In metal-mediated reactions, the aryl group with the least steric bulk is transferred.<sup>2</sup> In metal-free reactions, an *ortho*-substituted aryl group is sometimes transferred preferentially over a less hindered aryl moiety although electronic factors are also important.<sup>5c</sup> These steric and electronic effects often oppose one another, which make the chemoselectivity difficult to predict. Therefore, a detailed investigation into the chemoselectivity is currently being performed. A series of unsymmetric diaryliodonium salts was reacted with phenols, carboxylic acids and malonates (Figure 1) under metal-free conditions. The observed trends will be discussed.

**Figure 1.** Nucleophiles and diaryliodonium triflates used in the study



The difference in chemoselectivity can be demonstrated using the effects of having steric bulk in *ortho*-position employing a phenol and diethylmethyl malonate respectively as nucleophile acting on (phenyl)(*arene*)iodonium triflate, where the arene is *p*-tolyl or mesitylene. The mixtures obtained from the phenol were isolated in yields up to 84% in a 2.9:1 and 1:1.9 ratio respectively where the first number in each ratio is the phenyl group. Diethylmethyl malonate gave a different selectivity. The (phenyl)(*p*-tolyl)iodonium triflate gave the same 3:1 ratio towards transfer of the phenyl and the (phenyl)(mesityl)iodonium triflate gave a 99.8:0.2 ratio, also towards transfer of the phenyl, both isolated in 56% yield. Steric bulk in *ortho*-position can either hinder or facilitate transfer of that arene.

### ACKNOWLEDGEMENTS

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