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Efficient Arylation of Heteroatom Nucleophiles Using TMP-Iodonium(III) Salts

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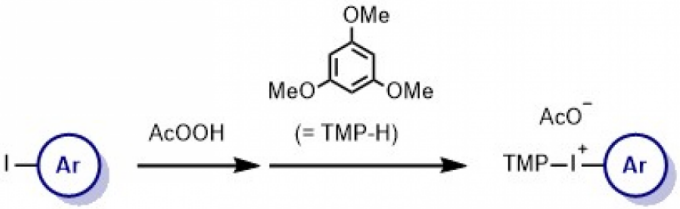
PURPOSE OF THE ABSTRACT

Aryl ether and arylamine derivatives are ubiquitous structures found in pharmaceutical products and organic functional materials. Considerable efforts have been devoted so far to the development of transition-metal-catalyzed coupling reactions forming aryl-heteroatom bonds. The severe drawback of these reactions is, however, the use of specific catalysts and a contamination of the products with metal traces. Diaryliodonium(III) salts are attractive arylating reagents, which induce various aryl-heteroatom bond formations under transition-metal-free conditions.[1] TMP-iodonium(III) salts, which consist of trimethoxyphenyl (TMP) group as one aryl group, lead to unified selective bond formation with the other aryl group.[2] Therefore, design of highly reactive TMP-iodonium(III) salt would provide an alternative green sustainable methods for metal-free arylation. Herein, we describe the efficient aryl-heteroatom bond formations using TMP-iodonium(III) salts for the arylation of heteroatom nucleophiles, such as phenols and amines.

Our group recently accomplished the facile synthesis of TMP-iodonium(III) acetate, which involves generation of aryliodine diacetate using peracetic acid followed by condensation with 1,3,5-trimethoxybenzene. This simple method enables synthesis of various TMP-iodonium(III) acetates in high yield, which are obtained as pure solid form by trituration with diethyl ether. The reaction of these TMP-iodonium(III) acetates with phenol derivatives proceeded to afford the corresponding diaryl ethers in high yields (up to >99%). The present O-arylation reaction was highly compatible with a wide variety of functional groups. Furthermore, protected amines, such as N-methoxy sulfonamide derivatives, were successfully arylated by using TMP-iodonium(III) acetates in high yields.

FIGURES



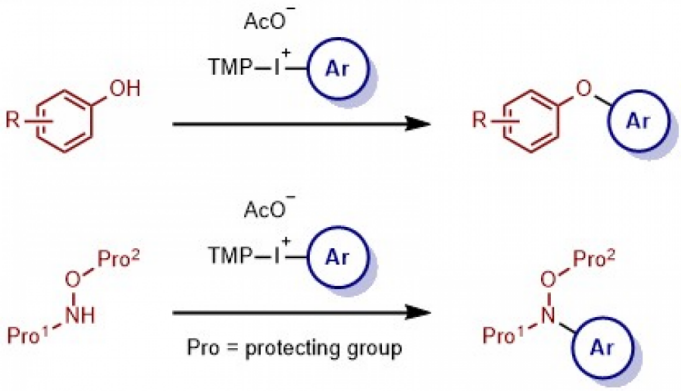


FIGURE 1

Synthesis of TMP-iodonium(III) acetate

TMP-iodonium(III) acetate can be obtained by simple conditions and procedure.

FIGURE 2

Aryl-heteroatom bond formation with TMP-iodonium(III) acetate

TMP-iodonium(III) acetate serve as efficient arylating reagent for various heteroatom nucleophiles under transition-metal-free conditions.

KEYWORDS

Hypervalent iodine(III) | Arylation | Transition-metal-free conditions

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