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Hypervalent Iodine-Mediated Synthesis of Sulfones Using Organozinc Pivalates and Sulfinate Salts

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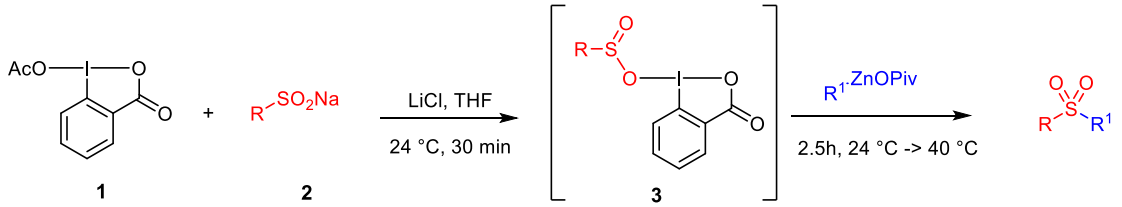
Sulfones are highly valuable organic molecules due to their widespread presence in pharmaceuticals, agrochemicals, biologically active compounds, and polymer materials. Beyond their prevalence in applied chemistry, they also serve as versatile synthetic intermediates in organic synthesis. The sulfone functional group can temporarily modulate chemical reactivity, enabling a wide range of transformations.[1,2] Common methods for sulfone synthesis include the selective oxidation of thioethers, electrophilic alkylation/arylation of sulfinate salts, and nucleophilic substitution of halides.[3] However, these methods often suffer from limitations such as narrow substrate scope and substitution patterns. In particular, the use of sulfonyl halides poses challenges due to their sensitivity to moisture, unpleasant odor, and poor functional group tolerance.

Our group previously investigated the umpolung reactivity of hypervalent iodine reagents (HIR), particularly the benziodoxolones, in the synthesis of amines, sulfonamides[6] and sulfinyl hydrazides.[7] In this work, we present a new approach to sulfone synthesis. By taking advantage of our know-how on the generation of sulfonyl-containing HIR intermediate, we achieved high to quantitative yields of diverse sulfones using stable sulfinate salts in combination with organozinc pivalates (Scheme 1). A

highlight of this work is the successful sulfonylation of various compounds using the rigid bicyclo[1.1.1]pentane sulfinate salt (BCP–SO_2Na), enabling efficient access to functionalized BCP-sulfones. Notably, this innovative approach allows for the in-situ generation of the sulfinate salt and shows excellent compatibility with subsequent transformations, making it well-suited for one-pot sulfone synthesis.



Scheme 1: General scheme for Sulfone Synthesis

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Short Bio

José Carlos Ferreira da Cunha is a PhD student in Sustainable Chemistry at MMMarques Research Group - Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, and at Bräse Research Group - Karlsruher Institut für Technologie (KIT), Germany.

His research focuses on development of innovative applications of novel hypervalent iodine reagents for sulfone and amine synthesis in batch and flow chemistry.

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