SYNLETT Spotlight 33

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

Samarium Diiodide

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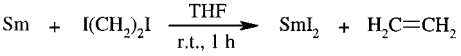
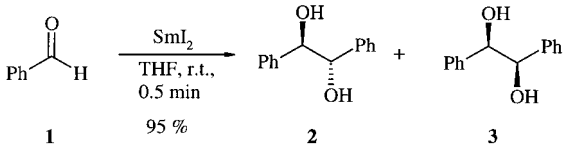
Introduction

First introduced in organic synthesis by Kagan and coworkers in the late 1970s,[1] samarium diiodide (SmI_2) has rapidly become a well-established reagent in preparative organic chemistry.[2] This powerful and versatile one-electron transfer reductant is commercially available, but can also be conveniently prepared from samarium and diiodoethane or diiodomethane as a solution in THF.[3] Its properties and reactivity can further be modified by addition of catalysts[4] and by solvent additives.[5] Samarium diiodide serves as a mild and selective reagent promoting a wide range of synthetically important transformations, such as reductions[6] and reductive coupling reactions.[2]

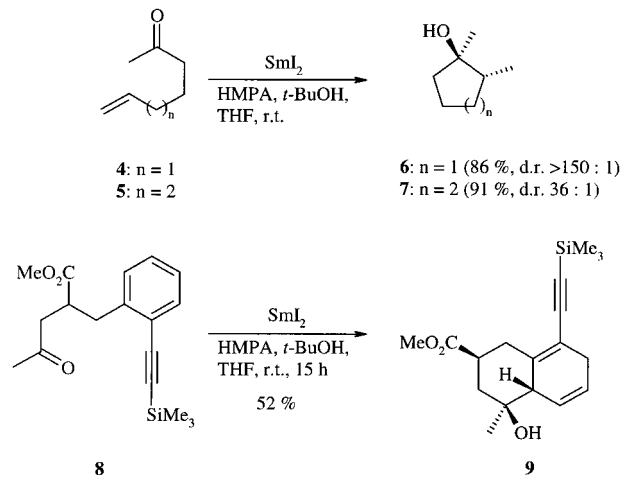


Abstracts

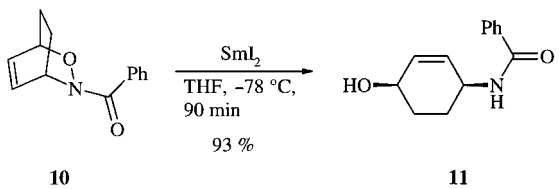
(A) By transferring an electron to aldehydes and ketones, SmI_2 generates ketyl radical anions, which can undergo pinacolic-coupling reactions. The addition of benzaldehyde **1** to a solution of SmI_2 in THF leads to its rapid reductive coupling affording **2** and **3** in high yield, but with poor diastereoselectivity (**2**:**3** = 1:1.3).[7] However, addition of polyethylene glycols such as tetraglyme increases the diastereoselectivity up to 6:1 in favour of the *erythro*-isomer **2**.[8]



(B) SmI_2-promoted intramolecular ketone-olefin coupling reactions offer a highly efficient way to cyclic and bicyclic systems. The utility of this method is not only due to the variety of ring sizes, which can be prepared, but also to the capacity of SmI_2 to promote sequential reactions.[2b,2d] SmI_2-mediated cyclisation of **4** and **5** in the presence of HMPA, which is necessary for efficient ketone-olefin coupling,[9] proceeds smoothly to afford cycloalkanols **6** and **7** in good yield and high diastereoselectivity favouring a *cis* relationship between the two methyl groups.[10] As an example for a novel 6-*trig* cyclisation the addition of **8** to a solution of SmI_2 and HMPA in THF results in the formation of hexahydronaphthalene derivative **9** in 52% yield as a single diastereomer.[11]



(C) SmI_2 can also be used for the reductive cleavage of carbon-heteroatom bonds or of N-O bonds in hydroxylamine derivatives and heterocycles. Subjecting **10** to a solution of SmI_2 in THF provides the amino alcohol **11** in excellent yield.[12]



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References and Notes

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