Diiodomethane: A Versatile C1 Building Block

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Introduction

Diiodomethane, better known as methylene iodide, is a dense (3.325 g/mL at 25 °C), light-sensitive, pale-yellow liquid. Because of its high density, it is used by the gemological industry to determine the density of minerals.1 Being such an interesting compound, diiodomethane is a versatile C1 building block, which can be used to form carbon–carbon and carbon–heteroatom bonds. It is an easy-to-handle compound and can be used in a wide number of different reactions such as epoxidation,2 diazotization,3 iodomethylation,4 cyclopropanation,5 alkene reduction,6 and sigmatropic rearrangement.7 In the presence of metallic samarium, the air-sensitive samarium diiodide (SmI2) is formed in situ; this is cheaper than buying samarium diiodide.8

Diiodomethane is commercially available, but can also be prepared by mixing methylene dichloride and sodium iodide in dimethylformamide at a constant temperature of 100 °C for 6–8 hours.9

Abstracts

(A) Alkylation of Diiodomethane
Bull and Charette reported an improved procedure to obtain functionalized gem-diiodoalkanes with acceptable functional group tolerance towards olefins, acetals, ethers, carbamates, and hindered esters.10

(B) β-Elimination of 2-Halogen-3-hydroxyesters and Synthesis of (Z)-Vinyl Halides
(Z)-α,β-Unsaturated esters were synthesized from 2-halo-3-hydroxyesters in good to excellent yields using a mixture of metallic samarium and diiodomethane. (Z)-Vinyl halides can be obtained with high diastereoselectivities and yields from O-acetylated 1,1-diiodo alcohols, metallic samarium, and diiodomethane in THF at room temperature.8

(C) Synthesis of 2,3-Dideuterioesters
The 1,4-reduction of α,β-unsaturated esters with D2O in the presence of metallic samarium and diiodomethane afforded the corresponding 2,3-dideuterioesters in good to excellent yields.6

(D) Transformation of Carbonyl Compounds into Epoxides
Epoxides are important because they can be opened by a variety of nucleophiles to afford 1,2-disfunctionalized systems. Concepción et al. reported a general, easy, and simple transformation of aldehydes and ketones into epoxides with excellent yields using diiodomethane and metyllithium at 0 °C.2
(E) Synthesis of (E)-α-Hydroxy-β,γ-unsaturated Amides
Concellón and co-workers\(^1\) reported an easy and simple procedure to prepare (E)-α-hydroxy-β,γ-unsaturated amides using metallic samarium and diiodomethane with high regio- and diastereoselectivity.

(F) Cyclopropanation
Cyclopropanation of alkenes can be carried out by a mixture of metallic samarium and diiodomethane.\(^1\) Cyclopropanation of terminal alkynes under the action of diiodomethane and triethylaluminum proceeded stereoselectively.\(^1\)

(G) Iodomethylation of Amino Aldehydes
The halomethylation of carbonyl compounds is difficult to achieve due to the instability of halomethyl lithium compounds. As an alternative, Bernad et al. reported a smoothly proceeding reaction using metallic samarium and diiodomethane.\(^6\)

(H) Double Carbonylation of Diiodomethane
Double carbonylation of diiodomethane in triethylorthoformate in the presence of catalytic amounts of rhodium complex gave diethylmalonate in good yield.\(^3\)

(I) Sigmatropic Rearrangement
Li and co-workers described an efficient method for the synthesis of β-diketones from aromatic α-bromo ketones in the presence of diiodomethane and diethylzinc. Aliphatic α-bromomethyl ketones gave 2,4-disubstituted furans or cyclopropanols in moderate yield.\(^7\)

(J) Diazotization for the Synthesis of Aryl Iodides
The reactions of aryl amines in the presence of isoamyl nitrite and sulfuric acid proceeded stereoselectively.\(^5\)

(K) Coupling Molecules with a CH₂ Linkage
In the synthesis of ditopic ligands, bispyrazolylpyridine molecules can be coupled with CH₂ linkages using sodium hydride and diiodomethane with high regio- and diastereoselectivity.

References
(9) Xu B., CN102020529-A, 2011.