**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 C\(_1\) 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 (SmI\(_2\)) 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**

(\(\text{E}\)-\(\text{α,β}\)-Unsaturated esters were synthesized from 2-halo-3-hydroxyesters in good to excellent yields using a mixture of metallic samarium and diiodomethane. (\(\text{Z}\))-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 D\(_2\)O 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-dirunctionalized systems. Concepcion et al. reported a general, easy, and simple transformation of aldehydes and ketones into epoxides with excellent yields using diiodomethane and methylthium at 0 °C.\(^2\)
(E) Synthesis of (E)-α-Hydroxy-β,γ-unsaturated Amides
Concèllon 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.\(^1,2\) Cyclopropanation of terminal alkenes under the action of diiodomethane and triethylaluminum proceeded stereoselectively.\(^3\)

(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.\(^4\) The reactions of aryl amines in the presence of isoamyl nitrite and \(\text{CH}_2\text{I}_2\) formed aryl iodides cleanly and in good yield.\(^3\)

(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.\(^1\)

(I) Sigmatropic Rearrangement
Li and co-workers described an efficient method for the synthesis of \(\beta\)-diketones from aromatic \(\alpha\)-bromo ketones using metallic samarium and diiodomethane.\(^5\) Double carbonylation of diiodomethane in triethylorthoformate in the presence of catalytic amounts of rhodium complex gave diethylmalonate in good yield.\(^1\)

(J) Diazotization for the Synthesis of Aryl Iodides
The reactions of aryl amines in the presence of isomyl nitrite and diiodomethane formed aryl iodides cleanly and in good yield.\(^6\)

(K) Coupling Molecules with a \(\text{CH}_2\) Linkage
In the synthesis of ditopic ligands, bispyrazolylpyridine molecules can be coupled with \(\text{CH}_2\) linkages using sodium hydride and diiodomethane in dichloromethane with moderate yields, as reported by Zadykowicz and Potvin.\(^1\)

References

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