SAMARIUM(II) IODIDE - HMPA: A VERY EFFICIENT SYSTEM FOR THE SELECTIVE REDUCTION OF α,β -UNSATURATED CARBONYL COMPOUNDS

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<u>Summary</u>: α,β -Unsaturated esters, acids, amides and an anhydride undergo efficient double bond reduction by SmI₂/HMPA in tetrahydrofuran.

Publications during the past fifteen years have demonstrated the versatility of samarium(II) diiodide as a reagent in organic chemistry.¹ Recent applications include the SmI₂ mediated vinylogous Barbier reaction,² the reduction of nitroalkanes to alkyl hydroxylamines,³ the reduction of esters, anhydrides, and amides to alcohols under basic conditions,⁴ and the conjugated reduction of α , β -unsaturated esters and amides.⁵ It is the latter report which prompts the present communication.

In late 1991, Inanaga and co-workers⁵ found that the system SmI_2 -N,N-dimethylacetamide (DMA) could reduce the double bond of α , β -unsaturated esters and amides, using an alcohol (usually t-butanol) as the proton source in tetrahydrofuran (THF). They stated that the use of hexamethylphosphoric triamide (HMPA) as an additive (instead of DMA) resulted in reductive dimerization as the predominant pathway, and a separate communication was published on this subject.⁶

Our observations are that HMPA is an excellent promoter, not only for the SmI_2 induced reduction (not reductive dimerization) of the double bond of α,β -unsaturated esters and amides, but also for mono and diacids (Table 1). Optimum conditions involve the reaction of the organic substrate with two equivalents of SmI_2 and either 2.3 or 9.2 equivalents of HMPA in THF. HMPA is not required for diacids where both acid functions are directly attached to the double bond, and maleic anhydride also reacts cleanly in the absence of HMPA. Note that these reactions proceed for di-, tri- and tetrasubstituted double bonds.

The following general procedure was used: to a solution of the α , β -unsaturated compound [0.25 mmol] in dry THF (2.0 mL) was added 0.5 mmol of a 0.1M SmI₂ solution in THF, and then HMPA (see Table 1 for proportions), under nitrogen. The reaction mixture was stirred at room temperature for 1 - 30 minutes, diluted with water and extracted with ether. The ether extract was dried (MgSO₄), passed through silica gel, and then concentrated to give the product. Further purification, if required, involved recrystallization or distillation. Note that for carboxylic acids, after dilution with water, 5% NaHCO₃ was added, followed by ether extraction. The aqueous phase was acidified [5% HCl], extracted with ether and the combined, dried (MgSO₄) ether extracts were worked-up as described above.

Substrate	HMPA, mmol	Reaction time, min.	Product	Yield ^b , %
Methyl methacrylate	0.57	30	Methyl 2-methylpropionate	67
Methyl cyclohexene-1 carboxylate	0.57 2.29	30 30	Methyl cyclohexanecarboxylate Methyl cyclohexanecarboxylate	10 64
Methyl crotonate	0.57	30	Methyl n-butyrate	59
Cinnamic acid	2.29	1	Hydrocinnamic acid	95
Methacrylic acid	2.29	1	2-Methylpropionic acid	80
C ₂ H ₅ CH=C-COOH CH ₃	2.29	30	2-Methylpentanoic acid	91
Ph(COOH)C=CH ₂	2.29	1.	PhCH(CH ₃)COOH	60
Maleic acid	-	5	Succinic acid	99
$\stackrel{\text{HOOC}}{\underset{H}{\longrightarrow}} \stackrel{\text{CH}_3}{\underset{\text{COOH}}{\longrightarrow}}$	-	5	HOOCCH2CH(CH3)COOH	88
(CH ₃) ₂ C=C ^{CH₂COO COOH}	OH 0.57	30	(CH ₃) ₂ CHCH(COOH)CH ₂ COOH	75
$Ph CH_2COOH$ $C = C$ $CH_3 COOH$	0.57	30	PhCH(CH ₃)CH(COOH)CH ₂ COOH	53
Maleic anhydride	-	5	Succinic anhydride	96
Cinnamide	0.57 2.29	30 1	Hydrocinnamide Hydrocinnamide	30 65

TABLE 1

HMPA Mediated Reduction of α,β-Unsaturated Carbonyl Compounds^a

^aConditions: substrate (0.25 mmol), SmI₂ (0.5 mmol), r.t. (N₂ atm.). ^bYields of isolated materials. Products were identified by comparison of spectral properties (ir, nmr, ms), and gc retention times with authentic samples.

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