Rapid and Mild Deoxygenation of Organoheteroatom Oxides with the Efficient Electron Transfer System SmI_2–Tetrahydrofuran–Hexamethylphosphoric Triamide

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A variety of organoheteroatom oxides such as sulphoxides, sulphones, *N*-oxides, a phosphine oxide, and an organo tin oxide were rapidly deoxygenated at room temperature by using a stoicheiometric amount of SmI_2 in tetrahydrofuran–hexamethylphosphoric triamide.

Although a number of methods have so far been developed for the deoxygenation of sulphoxides[1] and *N*-oxides,[2] only a few methods are available for the reduction of sulphones,[3] phosphine oxides,[4] or organotin oxides.[5]

Recently we have found that the addition of hexamethylphosphoric triamide (HMPA) markedly accelerates the electron transfer reaction of samarium di-iodide (SmI_2).[6,7] Here we report rapid and mild deoxygenation of sulphones, a phosphine oxide, and an organotin oxide as well as other organoheteroatom oxides by using the efficient electron transfer system of SmI_2–tetrahydrofuran (THF)–HMPA.[8]

At room temperature, sulphoxides,† aromatic sulphones, both aliphatic and aromatic amine *N*-oxide, and bis(tributyltin) oxide were reduced almost instantaneously. The addition of HMPA is crucial especially for the reduction of sulphones, triphenylphosphine oxide, or tributyltin oxide (Table 1).

It is noteworthy that aromatic sulphides can be protected in the form of the corresponding sulphones, since deoxygenation

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† Deoxygenation of diaryl and alkyl aryl sulphoxides by SmI_2 (without HMPA) has been reported (ref. 7); refluxing or a long reaction time was required: see Table 1.

Table 1. Deoxygenation of organoheteroatom oxides by SmI_2–THF–HMPA.[a]

Run	Heteroatom oxide	Temp/ °C	Time/ min	Product	Yield (%)[b]
1	$Ph_2S=O$	20	1	Ph_2S	94 (88)[c]
2	$PhS(=O)Me$	20	1	PhSMe	93
3	$Bu_2S=O$	20	1	Bu_2S	99 (71)[d]
4[e]	$Ph_2S(=O)_2$	20	1	Ph_2S	93 (0)[d]
5[e]	$PhS(=O)_2Me$	20	10	PhSMe	99 (0)[d]
6[e]	$Bu_2S(=O)_2$	65	8 h	Bu_2S	26
7	4-Methylmorpholine *N*-oxide	20	1	4-Methylmorpholine	98
8	Quinoline *N*-oxide	20	1	Quinoline	96
9	$Ph_3P=O$	65	16 h	Ph_3P	75 (0)[f]
10	$(Bu_3Sn)_2O$	20	1	$(Bu_3Sn)_2$	92 (0)[d,g]

[a] General procedure: to a mixture of the oxide (0.3 mmol) and HMPA (0.3 ml) was added SmI_2–THF (0.1 mol dm^{-3}; 6.6 ml, 6.6 mmol) under nitrogen. Then the reaction mixture, after dilution with hexane, was filtered through Florisil and purified by column chromatography on silica gel. [b] Isolated yield. Yields reported or obtained in the absence of HMPA after prolonged reaction time are in parentheses. [c] At 20 °C, 3 days (ref. 7). [d] At 20 °C, 24 h. [e] Reaction on 0.2 mmol scale using 8.8 mmol of SmI_2. [f] See ref. 7. [g] Hexabutylstannane (14%) was isolated.

of the latter rapidly regenerated the original sulphides under extremely mild conditions. Esters remained intact under the present conditions and, in some cases, sulphoxides were selectively reduced in the presence of ketones.‡

The mildness, convenience, and rapidity as well as high yields and wide applicability make the present deoxygenation method highly practicable, although the carcinogenic properties of HMPA should be considered.

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‡ *E.g.* the reduction of a mixture of diphenyl sulphoxide (0.3 mmol) and octan-2-one (0.3 mmol) with SmI_2 (0.66 mmol) at room temperature for 1 min afforded diphenyl sulphide and unchanged ketone almost quantitatively.

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