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A Mild and Convenient Method for the Reduction of Organic Halides by Using a SmI_2-THF Solution in the Presence of Hexamethylphosphoric Triamide (HMPA)

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A remarkable effect of HMPA was observed in the reduction of organic halides with a SmI_2-THF solution. Various types of organic halides were reduced rapidly to the corresponding alkanes in almost quantitative yields under mild reaction conditions.

The reduction of carbon-halogen bonds to C-H bonds is one of the important and well-established reactions in organic synthesis.[1)] In the course of our study utilizing SmI_2 in organic synthesis, it was found that the addition of HMPA strikingly promoted the reduction of organic halides by SmI_2-THF system originally developed by Kagan et al.,[2)] thus making the method much more valuable.

$$\mathrm{R-X} \xrightarrow[\text{THF-HMPA}]{\mathrm{SmI_2}} \mathrm{R-H} \qquad (\approx\text{quant})$$

As can be seen in the Table, the method is effective for prim-, sec-, and tert-alkyl, vinyl, and aromatic iodides, bromides, and even chlorides, the last ones having usually required fairly drastic conditions in the conventional methods.[1,2)] Ester function was not affected in the present reaction conditions. Particularly noteworthy is that when the reduction of 1-bromonaphthalene or 2-bromoadamantane was carried out in the presence of D_2O, no deuterated naphthalene was detected on the ^{13}C NMR spectrum, whereas 2-bromoadamantane afforded a mixture of 2-deuterated (ca. 80%) and non-deuterated adamantane (ca. 20%), suggesting that both radical[3)] and anionic species are involved in the reaction depending on the substrates used. It is important to note that enough amount of HMPA (ca. 5% of the SmI_2-THF solution) was found to be essential for the present reduction.[4,5)] The formation of a solvated electron[6)] may be crucial.

Convenience, mildness, and rapidity of the reaction and high yields of the products make the present method practically very attractive for the reduction of a wide range of organic halides. It should also be noted that the present reduction system provides an easy access to aryl radicals from the corresponding aryl iodides, bromides, or even chlorides under extremely mild conditions.[7)]

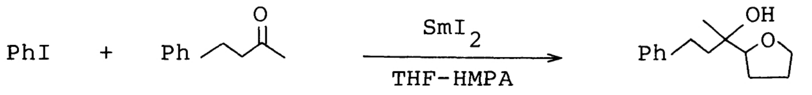
Table 1. Reduction of Organic Halides by a SmI_2-THF-HMPA Solution[a)]

Entry	Organic halide	Reaction conditions Temp, Time	Proton source	Yield/% of product[b)]
1	$\underline{n}$-$C_{10}H_{21}I$	RT, 5 min	2-PrOH	> 95
2	$\underline{n}$-$C_{10}H_{21}Br$	RT, 10 min	2-PrOH	> 95
3	$\underline{n}$-$C_{12}H_{25}Cl$	60 °C, 8 h	2-PrOH	> 95
4	iodocyclododecane	RT, 10 min	2-PrOH	> 95
5	bromocyclododecane	RT, 10 min	2-PrOH	> 95
6	cholesteryl chloride	RT, 3 h	2-PrOH, none	(99)
7	2-bromoadamantane	RT, 10 min	D_2O	(98)
8	1-bromoadamantane	RT, 10 min c)	2-PrOH, none	> 95
9	β-bromostyrene	RT, 20 min	none	> 95
10	1-iodonaphthalene	RT, 1 min	none	> 95
11	1-bromonaphthalene	RT, 5 min	D_2O, none	(98)
12	1-chloronaphthalene	RT, 15 min	none	> 95
13	$\underline{p}$-bromoanisole	RT, 8 h	2-PrOH	82
14	bromo-$\underline{p}$-xylene	RT, 15 h	2-PrOH	84
15	4-bromobiphenyl	RT, 1 h	none	> 95
16	2-bromobenzyl acetate	RT, 2 h	none	(97)

a) The reactions were carried out by using substrates (0.1—0.4 mmol), a SmI_2-THF solution (0.1 mol dm^{-3}, 2.5—8.5 ml, 2.5 equiv.), and HMPA (0.1—0.4 ml) in the presence or absence of proton source (0.11—0.44 mmol) under an atmosphere of nitrogen. b) GLC yield. Isolated yields are given in parentheses. c) A SmI_2-CH_3CN solution (0.1 mol dm^{-3}) was used in place of the SmI_2-THF solution.

References

1) For a review, see A.R.Pinder, Synthesis, 1980, 425.
2) P.Girard, J.L.Namy, and H.B.Kagan, J. Am. Chem. Soc., 102, 2693 (1980): 1-Iodododecane and 1-bromododecane was reduced therein without the addition of HMPA by a refluxing solution of SmI_2-THF to afford dodecane (6 h, 95% and 2 days, 82%, respectively) but 1-chlorododecane did not react at all after refluxing for 2 days.
3) Radical process may be supported from the following experiment, where the initially formed phenyl radical abstracted hydrogen from THF and a SmI_2- induced coupling reaction of the resulting THF radical with a ketone took place.



(≈50%)

4) When a SmI_2-THF solution was mixed with HMPA, immediate color change of blue-green to deep purple was observed, but an investigation concerning the electron spin state of this solution was not carried out.
5) The highly promoting effect of HMPA on other electron transfer reaction has recently been observed in photoreduction: See D.Belotti, J.Cossy, J.P.Pete, and C.Portella, Tetrahedron Lett., 26, 4591 (1985).
6) G.Fraenkel, S.H.Ellis, and D.T.Dix, J. Am. Chem. Soc., 87, 1406 (1965); H.Normant, Angew. Chem., Int. Ed. Engl., 6, 1046 (1967).
7) The conventional tributyltin hydride reduction of aryl halides (usually iodides) has been reported to give less satisfactory results: See, for example, A.L.J.Beckwith and W.B.Gara, J. Chem. Soc., Perkin Trans. 2, 1975, 795 and references cited therein.

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