CHEMISTRY LETTERS, pp. 2101-2102, 1987. © 1987 The Chemical Society of Japan

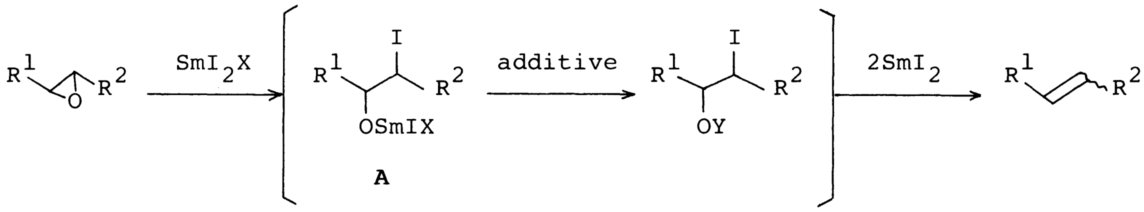
SmI_2-Induced Deoxygenation of Epoxides and Its Application to Carbonyl Methylenation in Combination with Iodomethylation[1)]

Mihaya MATSUKAWA, Takanori TABUCHI, Junji INANAGA,* and Masaru YAMAGUCHI
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki, Higashi-ku, Fukuoka 812

Deoxygenation of epoxides to olefins was effected by an efficient electron transfer system of SmI_2-THF-HMPA in the presence of N,N-dimethylaminoethanol (DMAE) or glutaric anhydride. This procedure, in combination with the SmI_2-induced iodomethylation, afforded a new, rapid and mild one-pot carbonyl methylenation method.

Based on our previous observation that the electron transfer from SmI_2 was highly promoted by co-existing HMPA,[2)] we have examined the deoxygenation of epoxides by using the SmI_2-THF-HMPA reduction system.[3)]

As can be seen in Table 1, it was found that the addition of DMAE or glutaric anhydride[4)] was necessary for rapid deoxygenation with high yields. The reaction mechanism is not clear, but the additives seem to serve as an activator of the oxygen atom for the elimination as shown in the following scheme: Initiation of the reaction may be oxirane ring-opening by a catalytic amount of Sm^{3+} species generated from SmI_2 by air-oxidation to give an intermediate (**A**), which was then protonated or acylated by additives to convert the alkoxide anion generated into a better leaving group (OY). Successive two-electron transfer causes reductive elimination to afford olefins.

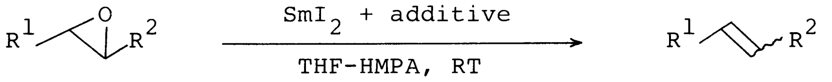


Deoxygenation of internal epoxides was not much accelerated except for one case (Run 7) where the participation of the neighboring acetoxy group was expected.

Since the present deoxygenation was found to be particularly useful for terminal epoxides, we then tried to combine the method with SmI_2-induced iodomethylation of carbonyl compounds,[5)] where species with the structure represented by **A** are considered to be formed as the primary products. As expected, rapid and mild one-pot carbonyl methylenation[6)] has been realized in good overall yields by the sequence of iodomethylation[5b)]-reductive elimination[7)] (Table 2).

For a typical experiment: To a mixture of cyclododecanone (18.2 mg, 0.1 mmol)

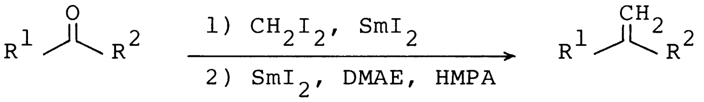
Table 1. Effect of Additives on the Dexygenation of Epoxides by SmI$_2$-THF-HMPA[a]



Run	Epoxide	Additive	SmI$_2$ (equiv.)	Reaction time/h	Yield/%[b]
1		none	1.2	2	37
2	〃	DMAE[c]	2	24	88
3	〃	DMAE	2	1.5	95
4	〃	glutaric anhydride	2	1	90
5		DMAE	2	24	95[d]
6	〃	glutaric anhydride	2	1	69[d]
7		DMAE	2	2.5	88[d]

a) To a mixture of epoxides (0.1 mmol), HMPA (0.1 ml) and additives (0.4 mmol) was added a SmI$_2$-THF solution (0.1 mol dm^{-3}) at room temperature under an atmosphere of nitrogen. b) Isolated yield. c) HMPA was not used. d) A mixture of isomers: E/Z ≈ 3/1 (by ^{1}H NMR analysis at 400 MHz).

Table 2. One-pot Carbonyl Methylenation by the Sequence of Iodomethylation-Reductive Elimination



Carbonyl compound	Reaction time/min		Isolated yield/%
	1st step,	2nd step	
CH$_3$(CH$_2$)$_{10}$CHO	5 ,	< 5	73
cyclododecanone	5 ,	< 5	80

and CH$_2$I$_2$ (16.1 µl, 0.2 mmol) in THF (0.5 ml) was added a SmI$_2$-THF solution (0.1 mol dm^{-3}, 4 ml) under an atmosphere of nitrogen. After stirring for 5 min at room temperature, DMAE (80 µl, 0.8 mmol), HMPA (0.3 ml), and a SmI$_2$-THF solution (4 ml) was added successively. Monitoring by TLC showed that the reaction completed within 5 min. Usual workup followed by chromatographic purification afforded methylenecyclododecane (14.5 mg, 80%).

References

1) Presented at the 54th National Meeting of the Chemical Society of Japan, Tokyo, April 1987.
2) K.Otsubo, J.Inanaga, and M.Yamaguchi, Tetrahedron Lett., 27, 5763 (1986); J.Inanaga, M.Ishikawa, and M.Yamaguchi, Chem. Lett., 1987, 1485; K.Otsubo, K.Kawamura, J.Inanaga, and M.Yamaguchi, ibid., 1987, 1487.
3) Deoxygenation of epoxides by SmI$_2$ (without HMPA) has been found by Kagan et al. for the first time; see P.Girard, J.L.Namy, and H.B.Kagan, J. Am. Chem. Soc., 102, 2693 (1980), where fairly long reaction time (2 days) was required.
4) Acyclic anhydrides could not be used since they were rapidly reduced under the conditions.
5) a) T.Imamoto, T.Takeyama, and H.Koto, Tetrahedron Lett., 27, 3243 (1986); b) T.Tabuchi, J.Inanaga, and M.Yamaguchi, ibid., 27, 3891 (1986).
6) For recent studies of carbonyl methylenation, see: K.Takai, Y.Hotta, K.Oshima, and H.Nozaki, Tetrahedron Lett., 1978, 2417; E.Murayama, T.Kikuchi, K.Sasaki, N.Sootome, and T.Sato, Chem. Lett., 1984, 1897; C.R.Johnson and B.D.Tait, J. Org. Chem., 52, 281 (1987).
7) Exposure of once isolated iodohydrins to the same reductive elimination conditions did not afford olefins in good yield but the major products were the corresponding alcohols formed by the replacement of iodine by hydrogen.

(Received August 7, 1987)