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Efficient Debromination of Vicinal α, β-Dibromo Carboxylic Acid Derivatives with the Sm/HOAc System

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Abstract: The , vicinal dibromo carboxylic acid and its derivatives were debrominated with Sm/HOAc system to afford the corresponding cinnamic acid and its derivatives in good yields under mild conditions.

Keywords: Debromination, vicinal dibromides, α, β-unsaturated carboxylic acid derivatives, Samarium.

The chemistry of samarium (II) iodide (SmI_2) is of current interest in organic synthesis. SmI_2 has been developed as a powerful, versatile and ether-soluble single-electron reductant and many examples have been reported of its use in the reduction of various functional groups[1]. Though SmI_2 is a useful reagent, storage is difficult because it is very sensitive to air oxidation. On the other hand, metallic samarium is stable in air and has strong reducing power ($Sm^{3+}/Sm=-2.41$ V). These properties have prompted the use of the more convenient and cheaper metallic samarium directly as a reductant instead of SmI_2. Recently, there have been reports on the direct use of metal samarium in organic synthesis[2].

The debromination of *vic*-dibromides to alkenes is important in organic synthesis as a deprotection reaction and some gentle methods (neutral, short reaction time, *etc*.) have been developed for this step[3]. However, examples where a samarium compound is used as a reagent for the debromination are very few. Yanada *et al.* has reported a debromination method with Sm in methanol[4], but the substrates were limited to aliphatic vicinal dihalides. Though they also examined the reductive debromination with Sm/HCl(cat.)[5], the systematic study on the debromination of α,β vicinal dibromo carboxylic acid derivatives has remained unexplored. Herein we wish to report an efficient method for the reductive debromination of α,β vicinal dibromo carboxylic acid derivatives with Sm/HOAc system.

The general procedure is as follows: under nitrogen atmosphere, into a mixture of the vicinal dibromide (1 mmoL) and Sm powder (0.30 g, 2 mmoL) in 2 mL of THF was

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added 0.5 mL of glacial acetic acid. The reaction mixture was stirred at room temperature until its color turned yellow (about 1 hour). Usual work-up gave the *trans* α, β-unsaturated carboxylic acid derivatives in good yields (see **Table 1** and **Scheme 1**). The products were characterized by ^{1}H NMR, IR and by comparison with authentic samples[8].

Scheme 1

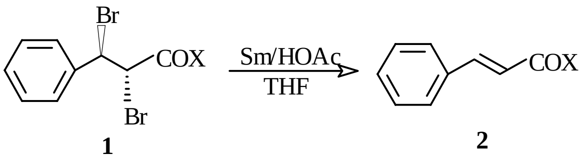

Table 1 Reductive debromination of the vicinal dibromides

Product	R	X	Isolated Yield (%)	MP (°C)	
				Found	Reported[6]
2a	H	OH	85	130-133	133-134
2b	H	OMe	92	32-34	34-36
2c	H	$OCH(CH_3)_2$	90	Oil	-
2d	H	$N(C_2H_5)_2$	95	65-68	67-69[7]
2e	*p*-MeO	OH	80	185-187	188-189.5
2f	*p*-MeO	OMe	82	91-93	94-95
2g	*p*-Me	OMe	86	53-55	55-56
2h	*o*-Cl	OMe	89	Oil	-

In conclusion, with high yields, mild reaction conditions and simple procedure, the present work may provide a useful method for debromination of α, β-dibromo-carboxylic acid derivatives. Further applications of the Sm/HOAc system are now in progress in our laboratory.

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References and Notes

1. (a) H. B.Kagan, J. L Namy, *Tetrahedron*, **1986**, *42*, 6573.
   (b) G. A. Molander, *Chem. Rev.*, **1992**, *92*, 29.
   (c) G. A. Molander, C. R. Harris, *Chem. Rev.*, **1996**, *96*, 307.
2. (a) Z. Hou, Y. Fujiwara, H. Taniguchi, *J. Org. Chem.*, **1988**, *53*, 3118.
   (b) A. Ogawa, T. Nanke, N. Takami, Y. Sumino, I. Ryu, N. Sonoda, *Chem. Lett.*, **1994**, 379.
   (c) Y. Kamochi, T. Kudo, *Chem. Pharm Bull.*, **1994**, *42*, 402.
3. (a) S. G. Davies, S. E. Thomas, *Synthesis*, **1984**, 1027.
   (b) K. Yanada, R. Yanada, H. Meguri, *J. Chem. Soc., Chem. Commun.*, **1990,** 730 and references cited therein.
4. R. Yanada, N. Negoro, *Tetrahedron Lett.*, **1996**, *37*, 9313.
5. R. Yanada, K. Bessho, K. Yanada, *Chem. Lett.*, **1994**, 1279.
6. J. Buckingham, *Dictionary of Organic Compounds*, Chapman and Hall, New York, 5th ed., **1982**.
7. H. G. O. Becker, K. F. Funk, *J. Prakt. Chem.* **1961**, *14*, 55.
8. The spectral data of Compounds **2a-2h** were submitted to editorial office of CCL.

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