

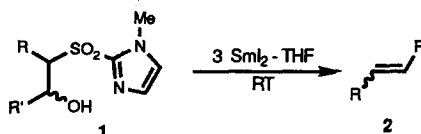
AN IMPROVED VARIANT OF THE JULIA OLEFIN SYNTHESIS:
REDUCTIVE ELIMINATION OF β -HYDROXY IMIDAZOLYL SULFONES
BY SAMARIUM DIIODIDE

Andrew S. Kende* and José S. Mendoza

Department of Chemistry
University of Rochester
Rochester, New York 14627 USA

SUMMARY: The reductive elimination reaction of β -hydroxy imidazolyl sulfones **1** to afford the corresponding olefins can be accomplished under mild conditions and in good yields using SmI_2 , offering a convenient modification of the Julia olefin synthesis.

The reductive elimination reaction of β -hydroxy sulfones to olefins has long been recognized as a very useful synthetic transformation and is commonly effected using sodium amalgam.¹ In this communication, we report a general method for this transformation employing a β -hydroxy imidazolyl sulfone and the efficient electron transfer system, SmI_2 -THF.²



The β -hydroxy imidazolyl sulfone derivatives were readily prepared using commercially available starting materials (Scheme 1). Thus, reaction of alkyl halide **3** with 2-mercapto-1-methylimidazole, Et_3N in THF afforded the sulfide **5**, which then was treated with mCPBA to give the corresponding sulfone. Base promoted addition of sulfone **6** to the aldehyde gave the diastereomers **1** in good yields.³

Scheme 1

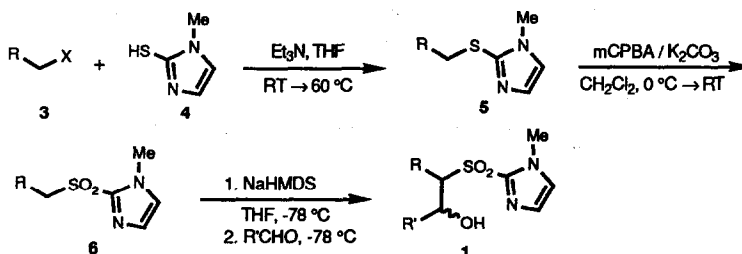
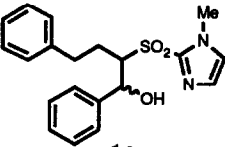
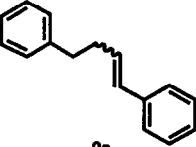
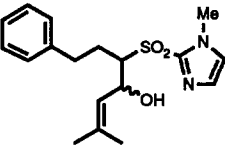
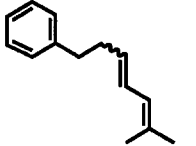
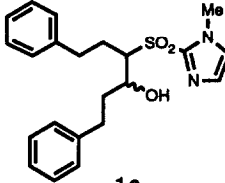
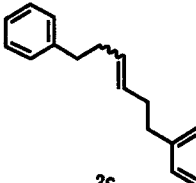
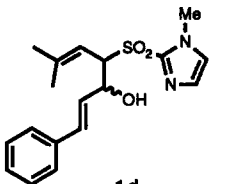
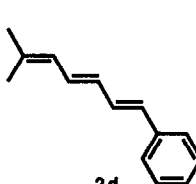
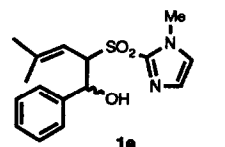
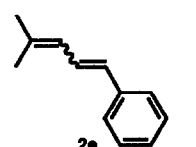


Table 1. Reductive Elimination of β -Hydroxy Imidazolyl Sulfones^a

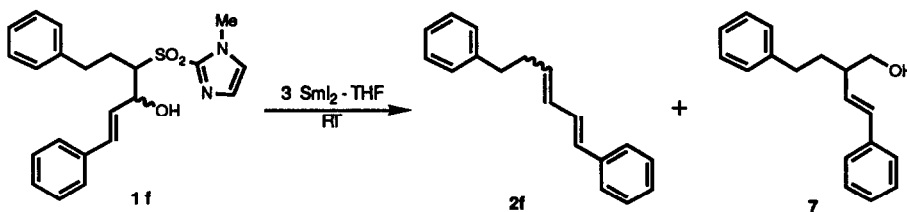
Entry	β -Hydroxy sulfone	Product (s) ⁵	Yield, ^b %	E/Z ratio ^c
1	 1a	 2a	82	8 : 1
2	 1b	 2b	84	5 : 1
3	 1c	 2c	55	3 : 1
4	 1d	 2d	78 ^d	
5	 1e	 2e	87	5 : 1

(a) For the standard procedure, see the text. (b) Yields were not optimized. All yields refer to purified compounds. (c) Determined by ¹H-NMR (300 MHz) analysis after silica gel chromatography. (d) Only this isomer was isolated.

As shown in Table 1, a variety of β -hydroxy imidazolyl sulfones undergo reductive elimination at room temperature on addition of the substrate in THF to a solution of freshly prepared SmI_2 in THF.⁴ Reactions proceed smoothly within minutes, and simple workup of the reaction mixture allows generation of the corresponding olefins in good yields.

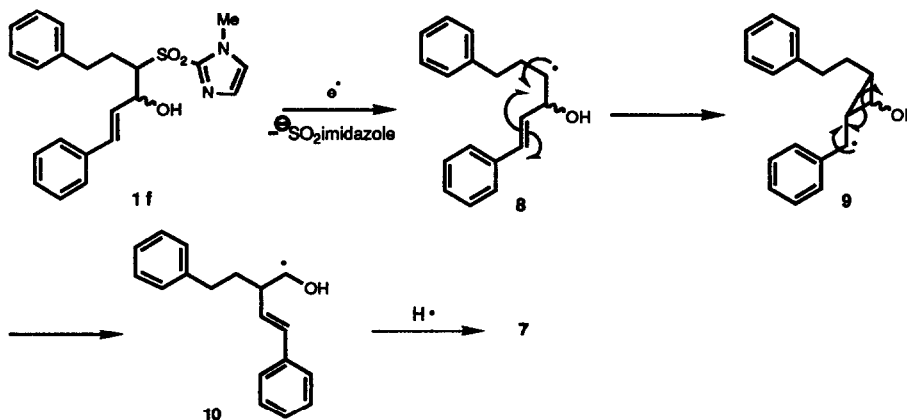
A typical procedure for the SmI_2 reaction is as follows (entry 1 in the Table): To a stirred solution of SmI_2 (1.5 mmol) in THF (12 ml) was rapidly added a solution of the β -hydroxy sulfone **1a** (0.185 g, 0.5 mmol) in THF (6 ml) under an argon atmosphere. After 15 min at room temperature the reaction mixture was still blue, due to excess of SmI_2 . The reaction mixture was then poured into a 10% solution of $\text{Na}_2\text{S}_2\text{O}_3$ (20 ml) and extracted with ethyl acetate. The residue was chromatographed over silica gel (hexane-ethyl acetate, 99:1) to give 0.085 g (82%) of **2a** as an 8:1 mixture of E/Z olefins.⁵

When the β -hydroxy imidazolyl sulfone **1f** was subjected to the above conditions, the expected diene **2f** was isolated in only 20% yield as a 9:2 mixture of E, E/E, Z isomers. Surprisingly, the rearranged homoallylic alcohol **7** was obtained as the major product in 48% yield.⁶

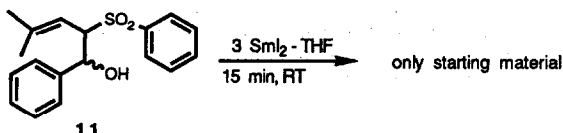


We tentatively rationalize this transformation as a one electron transfer process (Scheme 2). We envision that the initial step in the reduction mechanism closely resembles that of metal reduction of β -substituted sulfones.⁷ Thus, reaction of SmI_2 with the sulfone generates the radical anion, which upon loss of the imidazolesulfinate anion forms radical **8**. This then adds to the double bond to yield benzylic radical **9**. The latter subsequently reopens to generate the alkyl radical **10** which may be quenched by H^\cdot transfer from the solvent to afford the homoallylic alcohol **7**.⁸ However, more detailed studies are needed to confirm the mechanism and to explore the scope of this interesting transformation.

Scheme 2



The reductive elimination reaction of the β -hydroxy phenyl sulfone **11** was also attempted for comparison. In this case, however, the reaction conditions used for the reductive elimination of β -hydroxy imidazolyl sulfones were not effective and only traces of the desired diene could be detected by TLC.⁹



In a direct comparison of the Na(Hg) and SmI_2 methods, we found that treatment of the hydroxy sulfone **1c** with an excess of Na(Hg) 6% in THF/MeOH (1:1) at -35°C afforded a 1.3:1 mixture of E/Z olefins in less than 30% yield. Thus the present approach can provide an efficient route for preparing a variety of olefins under mild conditions, using readily available starting materials, and may be used as an alternative to the conventional Julia sequence.

Acknowledgment: Partial support of this research by grant CA-18846, awarded by the National Cancer Institute, is gratefully acknowledged.

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3. (a) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. (b) Hirai, K.; Matsuda, H.; Kishida, Y. *Tetrahedron Lett.* **1971**, 4359. (c) Kotake, H.; Yamamoto, T.; Kinoshita, H. *Chem. Lett.* **1982**, 1331.
4. Our reagent was prepared by modification of Kagan's procedure: Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. To a mixture of samarium powder (1.9 mmol) and 1,2-diiodoethane (1.5 mmol) was added THF (12 ml) under argon. An induction period was observed within a few minutes. After the reaction mixture was stirred at room temperature for 1 h an intense blue-green solution of SmI_2 was obtained. A solution of the substrate in THF was added to the above solution.
5. Satisfactory spectral data (IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and MS) have been obtained for all compounds. The NMR spectra of our products **2a**, **2b**, **2c**, and **2e** were in agreement with those given in the literature: (**2a**) Snider, B. B.; Jackson, A. C. *J. Org. Chem.* **1983**, *48*, 1471; Reich, H. J.; Chow, F.; Shah, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 6638. (**2b**) Vedejs, E.; Fang, H. W. *J. Org. Chem.* **1984**, *49*, 210; Reich, H. J.; Wollowitz, S. *J. Am. Chem. Soc.* **1982**, *104*, 7051. (**2c**) Descotes, G.; Chevalier, P.; Sinou, D. *Synthesis* **1974**, 364. (**2e**) Mathias, R.; Weyerstahl, P. *Chem. Ber.* **1979**, *112*, 3041; Miyaura, N.; Yamada, K. Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972; Reich, H. J.; Shah, S. K.; Chow, F. *J. Am. Chem. Soc.* **1979**, *101*, 6648.
6. Compound **7**: IR (CHCl_3) 3580, 3450, 3060, 3005, 2940, 1600, 1500 and 1450 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.43-7.20 (10 H, m), 6.55 (1H, d, $J = 15.9$ Hz), 6.06 (1H, dd, $J = 15.9, 8.9$ Hz), 3.72-3.58 (2H, m), 2.80-2.60 (2H, m), 2.54-2.40 (1H, m), 1.94-1.82 (1H, m), 1.78-1.62 (1H, m), 1.60 (1H, br s); $^{13}\text{C-NMR}$ (300 MHz, CDCl_3) δ 142.07, 136.99, 133.04, 131.01, 128.58, 128.40, 128.36, 127.46, 126.19, 125.82, 66.03, 45.89, 33.38, 32.83; MS m/e 252 (M^+).
7. The mechanism of the reductive elimination of β -benzoyloxy sulfones using sodium amalgam has been proposed as proceeding through a radical mechanism, see: Kocienski, P. J.; Lythgoe, B.; Waterhouse, I. J. *Chem. Soc., Perkin Trans. 1* **1980**, 1045.
8. For further information on the electron transfer chemistry of SmI_2 -THF, see ref. **2a**, **b**. Also, see: (a) Ujikawa, O.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1989**, *30*, 2837. (b) Collin, J.; Dallemer, F.; Namy, J. L.; Kagan, H. B. *Tetrahedron Lett.* **1989**, *30*, 7407.
9. The reaction mixture was quenched after standing at room temperature for 5 days. $^1\text{H-NMR}$ (300 MHz, CDCl_3) showed a 1.5:1 mixture of starting material/product. The product was shown to be a 6:1 mixture of E/Z olefins.

(Received in USA 27 August 1990)