This article was downloaded by: [McMaster University] On: 18 November 2014, At: 12:52 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

The Reductive Desulfonylation of β-Ketosulfones with TiCl₄/Sm System

Junquan Wang ^a & Yongmin Zhang ^a ^a Department of Chemistry, Hangzhou University, Hangzhou, 310028, P.R. China Published online: 21 Aug 2006.

To cite this article: Junquan Wang & Yongmin Zhang (1996) The Reductive Desulfonylation of β -Ketosulfones with TiCl₄/Sm System, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:10, 1931-1934, DOI: <u>10.1080/00397919608003547</u>

To link to this article: http://dx.doi.org/10.1080/00397919608003547

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages,

and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

THE REDUCTIVE DESULFONYLATION OF β -KETOSULFONES WITH TiCl₄/Sm SYSTEM

Junquan Wang Yongmin Zhang[•] Department of Chemistry, Hangzhou University, Hangzhou, 310028, P. R. China

ABSTRACT: β -Ketosulfones can be readily desulfonylated with TiCl₄/ Sm system to give corresponding ketones in acceptable yields in THF under mild conditons.

Since β -ketosulfones can be prepared in good yield by the acylation of sulfonyl carbanions with carboxylic acid chlorides and esters⁽¹⁾ or by the phase-transfer-catalysed reaction of corresponding halides with sodium arylsulfinates^(2,3) as well as α -alkylation reactions of β -keto sulfones can be readily accomplished^(4,5), the reduction of β -ketosulfones to corresponding ketones is a useful transformation, particularly in regioselective ketone alkylation. As a result many reagents have been used for the reductive dcsulfonylation of β -ketosulfones, such as zinc metal in acetic acid⁽⁶⁾, Al-Hg amalgam⁽⁷⁾, samarium diiodide SmI₂⁽⁸⁾, tributytin hydride (n-Bu)₃SnH⁽⁹⁾, sodium dithionite Na₂S₂O₄⁽¹⁰⁾and sodium hydrogen telluride NaHTe⁽¹¹⁾, etc.

Over the last two decades, low-valent titanium reagents⁽¹²⁾ have been of great interest in organic synthesis. We have recently reported

Copyright © 1996 by Marcel Dekker, Inc.

To whom correspondence should be addressed

O ArCCHS R	SO₂A	TiCl ₄ /Sm/THF	O ∥ ► ArCCH₂R +A	.r'SSAr' (minor product)
••		Ar	Ar'	R
	(a)	C ₆ H ₅	C ₆ H ₅	н
	(b)	C₅H₅	p-CH ₃ C ₆ H ₄	н
	(c)	p-ClC6H4	C ₆ H ₅	н
	(d)	p−BrC₀H₄	C ₆ H ₅	н
	(e)	p-CH ₃ C ₆ H ₄	C₅H₅	н
	(f)	C ₆ H ₅	C ₆ H ₅	CH₃
	(g)	C ₆ H ₅	C ₆ H ₅	C ₂ H ₅
	(h)	C ₆ H₅	C ₆ H ₅	C ₆ H ₅ CH ₂
			Scheme	

the reductive deoxygenation of sulfoxides⁽¹³⁾ and reductive coupling of arylsulfonyl chlorides and sodium arylsulfinates to corresponding diaryldisulfides⁽¹⁴⁾ with TiCl₄/Sm system. Herein we wish to report a novel method for the desulfonylation of β -ketosulfones with TiCl₄/Sm system. In our experiment work, we have found that α -unsubstituted - β -ketosulfones were easily desulfonylated to give corresponding ketones with TiCl₄/Sm system in THF at room temperature, while the reductive desulfonylation of α -alkyl- β -ketosulfones were achieved at refluxing temperature. Disulfides were also obtained as by-product. Some results were summarized in the Table.

Experiment Section

Melting points were uncorrected. The solvent tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to its use.

Entry	reaction condition temperature/time (°C) (h)	m.p(°C)	yield*(%)	¹ Η NMR(CDCl ₃),δ(ppm)
a	r. t/4	oil	65	2.5(s,3H), 7.2-7.9(m, 5H)
ь	r.t/4	oil	67	2. 5(s,3H),7. 2-7. 8(m,5H)
c	r. t/4	oil	62	2. 6(s,3H), 7. 2-7. 8(m,4H)
d	r. t/4	48-50	61	2. 5(s,3H), 7. 4-7. 8(m,4H)
e	r. t/4	oil	59	2. 3(s,3H),2. 5(s,3H), 7. 0-7. 8(m,4H)
f	refulxing/2	ગાં	56	1. 0-1. 4(t, 3H), 2. 7-3. 2(q, 2H), 7. 2-8. 0(m, 5H)
g	refulxing/2	oil	51	0. 8-1. 2(t,3H), 1. 4-2. 1(m,2H),2. 7-3. 0(t,2H), 7. 2-8. 1(m,5H)
h	refluxing/2	67-69	50	2. 7-3. 4(m,4H),7. 1-8. 1(m,10H)

Table. Physical and spectral data of the ketones

* Yields of isolated product.

¹H NMR spectra were recorded on a JEOL JOM-PMX 60 SI (60MHZ)instrument using TMS as internal standard.

General procedure for the reductive desulforylation of β -ketosulfones:

Under an inert atmosphere of nitrogen, 1. 14g (6mmol) TiCl₄ was added by syringe to a stirred slurry of 0. 3g (2mmol) powdered samarium in 20ml THF in a 50ml three-neck flask. The mixture was stirred magnetically for lh at room temperature. A light blue suspension was obtained. Then β -keto sulfones (1mmol) was added to this stirred suspension in one portion under an atmosphere of nitrogen. The mixture was stirred at room temperature or under refluxing conditions. The end of reactions was detected by TLC. A dilute solution of HC1(5%, 10ml) and ether (20ml) were added. The organic layer was seperated and the aqueous layer was extracted with ether (20ml). The combined organic solution was washed with water (20ml×2) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel (cyclohexane/acetate as eluent).

In view of the acceptable yield, simple experimental procedure, mild and neutral conditions, the present procedure offers an alternative to the methods for the desulfonylation of β -ketosulfones.

Acknowledgement : We are grateful to the National Natural Science Foundation of China for financial support.

References

- 1. Bartlett, P. A., Green, F. R., and Rose, E. H., J. Am. Chem. Soc., 1978,100,4852.
- 2. Veermstra, G. E., Synthesis, 1975, 519.
- 3. Wildeman, J., ibid., 1979, 733.
- 4. Samuelsson, B., Lamm, B., Acta Chem. Scand., 1971, 25, 1555.
- 5. Huang, X., Pi, J. H., Huaxue Shiji, 1992, 14(6), 321.
- 6. House, H. O., Larson, J. L., J. Org. Chem., 1968, 33,61.
- Mussato, M. C., Savoia, D., Trombini, c., and Ronchi, A. U., J. Org. Chem., 1980, 45, 4002.
- 8. Molander, G.A., Hahn, G., J. Org. Chem., 1986, 51(7), 1135.
- 9. Smith, A. B., Hale, K. J., and McCauley, J. P., Tetrahedron Lett., 1989, 30,5579.
- 10. Harris, A. R., Mason, T. J., Hannah, G. R., J. Chem, Res. (S)., 1990,7,218.
- 11. Huang, X., Pi, J. H., Synth. Commun., 1990, 20(15), 2297.
- 12. McMurry, J. E., Chem. Rev., 1989, 89, 1513.
- 13. Wang, J.Q., Zhang, Y.M., Synth. Commun., in press.
- 14. Wang, J.Q., Zhang, Y.M., Synth. Commun., in press.

(Received in the UK 31st October 1995)