This article was downloaded by: [University of Chicago Library] On: 12 August 2013, At: 05:51 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: <u>http://www.tandfonline.com/loi/lsyc20</u>

Aldol Condensation of β-Diketones and β-Ketoesters with Aldehydes Catalyzed by Samarium (III) Iodide

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

To cite this article: Weiliang Bao , Yongmin Zhang & Jingang Wang (1996) Aldol Condensation of β -Diketones and β -Ketoesters with Aldehydes Catalyzed by Samarium (III) Iodide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:16, 3025-3028, DOI: 10.1080/00397919608004607

To link to this article: http://dx.doi.org/10.1080/00397919608004607

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 <u>http://www.tandfonline.com/page/terms-and-conditions</u>

ALDOL CONDENSATION OF β-DIKETONES AND β-KETOESTERS WITH ALDEHYDES CATALYZED BY SAMARIUM (III) IODIDE

Weiliang Bao, Yongmin Zhang*, Jingang Wang

Department of Chemistry, Hangzhou University Hangzhou, 310028, P.R.China

Abstract: Catalyzed by SmI₃ β -diketones and β -ketoesters condense with aldehydes to give benzylidene substituted β -diketones and β -ketoesters at room temperatures in fair yields.

Organolanthanide chemistry is now in rapid evolution. Compared with the application of samarium(II) species in organic synthesis, little application of samarium(III) species was developed in organic synthesis¹. Nevertheless the reports of using samarium(III) in organic chemistry are rapidly increased recently. We reported that promoted by SmI₃ α -haloketones can react with aldehydes to give α , β -unsaturated ketones². Sasai reported that 1-chloro-2-heptanone is able to react with benzaldehyde to form α -chloro- β -hydroxy ketones at catalysis of Sm(HMDS)₃³; at the aid of Sm(OTF)₃ and s-BuLi methyliodide has been added to carbonyl group of acetophenone⁴; similarly catalyzed by Sm(OTF)₃ benzyl

Copyright © 1996 by Marcel Dekker, Inc.

amine can add to ethyl crotonate to form β -amino esters⁵: Mori reported that α haloketones may react with α -ketocarboxylates and α -diketones mediated by SmI₂ or SmI₃ to obtain α -hydroxy- γ -ketocarboxylates and 2-hydroxy-1,4-diketones respectively⁶. Very recently, we found that β -diketones can be synthesized via reaction of α -haloketones with acid chlorides or acid anhydrides at the aid of SmI₂ or SmI₃⁷.

Here we wish to report that mediated by Sml_3 , β -diketones can condense with aldehydes to form benzylidene-substituted β -diketones in fair yield:



 β -Ketoesters can also condense with aldehydes at the same conditions to give benzylidene-substituted β -ketoesters, but the yields are comparatively low:



TABLE 1. Reaction Conditions and Yields with β -Diketone

Entry	Aldehydes	Reaction	Yield(%)	
	Times(h)			
1	H-C ₆ H ₄ CHO	3	78	
2	p-Br-	3	72	
3	m-Br-	3	81	
4	p-Cl-	3	85	
5	p-CH ₃ -	3	90	
6	m-CH ₃ -	3	85	
7	Cinnamaldehyde	3	89	

Entry	Aldehydes	Reaction	Yield(%)
		Times(h)	
1	<mark>н-с</mark> ₆ н₄сно	3	75
2	р-СН ₃ -	3	80
3	m-CH ₃ -	3	75
4	m-Br-	3	70
5	Cinnamaldehyde	3	72

TABLE 2. Reaction conditions and Yield with B -Ketoesters

Generally such an Aldol condensation is performed at the catalysis of bases such as piperidine⁸ for several days. We conducted the reaction in neutral, mild conditions and only for several hours. The products are characterized fully by ¹H NMR and IR spectra.

Experimental

¹H-NMR spectra were recorded in CCl₄ on JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a PE 683 spectrometer. SmI₃ is prepared previously by samarium powder and iodine in dried THF.

General Procedure For The Condensation of β -Diketones And β - Ketoesters With Aldehydes: To a solution of SmI₃ (2mmol, in 20ml THF) are added benzaldehyde (4mmol) and acetylacetone or aceto acetate (4mmol) sequentially. After stirred at room temperatures for 3hr, the solution is treated with dilute hydrochloric acid (0.1M, 1ml) and extracted with ether (30ml × 2). The organic layer is washed with aqueous sodium thiosulfate solution and brine sequentially, dried over magnesium sulfate. The solvents are evaporated in vaccum. The products are separated by preparative TLC (silica gel) with cyclohexane and ethyl acetate (5:1) as eluent.

Acknowledgment: We thank the National Natural Science Foundation of China and Acadenia Sinica for financial supports.

References

3028

- Molander, G. A., In Comprehensive Organic Synthesis; Trost, B. M., Fleming, 1 Eds. Pergamon; Oxford, 1991; Vol.1, pp.251-282.
- 2. Yu, Y., Lin, R. and Zhang, Y., Tetrahedron Lett., 1993, 34, 4547.
- 3. Sasai, H., Arai, S., Shibasaki, M., J. Org. Chem., 1994, 59, 2661.
- 4. Fukuzawa, S., Tsuchimoto, T., Kanai, T., Chem. Letters, 1994, 1981.
- 5. Matsubara, S., Yoshioka, M., Utimoto, K., Chem. letters, 1994, 827.
- Arime, T., Kato, N., Komadate, F., Saegusa, H., Mori, N., Synth. Commun., 1994, 24, 3315.
 - b). Arime, T., Takahashi, H., Kobayashi, S., Yamaguchi, S., Mori, N., Synth. Commun., 1995, 25, 389.
- 7. Ying, T., Bao, W., Zhang, Y., Synth. Commun., in press.
- 8. Mcentee, M. E., Pinder, A. R., J. Chem. Soc., 1957, 4419.

(Received in the UK 02 February 1996)