

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/lcyc20>

A FACILE ONE-POT SYNTHESIS OF METHYL(2E)-2-METHYLALK-2-ENOATES FROM BAYLIS-HILLMAN ADDUCTS UNDER MICROWAVE IRRADIATION

Subramanian Ravichandran ^a

^a School of Chemistry, University of Hyderabad , Hyderabad, 500 046, India

Published online: 09 Nov 2006.

To cite this article: Subramanian Ravichandran (2001) A FACILE ONE-POT SYNTHESIS OF METHYL(2E)-2-METHYLALK-2-ENOATES FROM BAYLIS-HILLMAN ADDUCTS UNDER MICROWAVE IRRADIATION, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:13, 2055-2057, DOI: [10.1081/SCC-100104425](https://doi.org/10.1081/SCC-100104425)

To link to this article: <http://dx.doi.org/10.1081/SCC-100104425>

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>

SYNTHETIC COMMUNICATIONS, 31(13), 2055–2057 (2001)

A FACILE ONE-POT SYNTHESIS OF METHYL(2E)-2-METHYLALK-2-ENOATES FROM BAYLIS-HILLMAN ADDUCTS UNDER MICROWAVE IRRADIATION

Subramanian Ravichandran

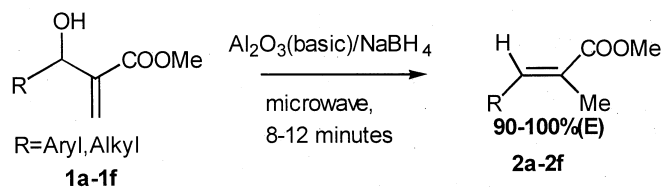
School of Chemistry, University of Hyderabad,
Hyderabad-500 046, India

ABSTRACT

A facile procedure for the synthesis of the title compound is described.

In connection with our research on the Baylis-Hillman reaction,^{1–3} I herein report a simple and efficient methodology for the stereoselective synthesis of methyl(2E)-2-methylalk-2-enoates from Baylis-Hillman adducts using basic Al_2O_3 and NaBH_4 under microwave irradiation.^{4–6} The synthetic scheme employed is outlined below. The experimental result is given in the table 1.

The [E]-selectivity in these reactions can be possibly explained on the basis of a mechanism proposed by our research group.⁷ Although I did not



Scheme 1.

Table 1. Synthesis of Methyl(2*E*)-2-methylalk-2-enoates^{a,b}

Substrate	R	Power (%)	Time ^d (minutes)	T ^f /°C	Product	Yield (%) ^c	<i>E:Z</i> ^e
1a	C ₆ H ₅	10	10	165	2a ⁹	90	95:05
1b	4-MeC ₆ H ₄	10	10	129	2b	80	95:05
1c	4-ClC ₆ H ₄	10	10	131	2c	83	100:0
1d	2-ClC ₆ H ₄	10	10	100	2d	81	95:05
1e	2,4-ClC ₆ H ₄	10	08	170	2e	81	94:06
1f	n-propyl	10	12	173	2f	72	90:10

^aAll reactions were carried out on a 5 mM scale of the alcohol (**1a–1f**) with basic Al₂O₃ (5 mM) and NaBH₄ (5 mM) under microwave irradiation.

^bSatisfactory spectral data were obtained for all compounds.

^cIsolated yields of the product after column chromatography (1% EtOAc in hexane).

^dThe reaction completed within the time specified in the table.

^eStereochemical assignments and isomeric purities were based on difference in chemical shifts and integration ratios of olefinic protons in ¹H NMR analysis.

^fFinal temperature reached by the reaction mixture.

encounter any accident during these studies, I recommend extreme caution for reactions on larger scale.

In summary I have developed a facile and practical method for the stereoselective synthesis of methyl(2*E*)-2-methylalk-2-enoates using a solventless system, basic Al₂O₃ and NaBH₄ with 3-hydroxy-2-methylenealkanoates under microwave irradiation.

EXPERIMENTAL

General

All the required Baylis-Hillman products were obtained by the reaction of the corresponding aldehydes with methyl acrylate in the presence of a catalytic amount of DABCO according to the literature procedure.⁸

General Procedure

NaBH₄ (0.189 g, 5 mM) and basic Al₂O₃ (0.509 g, 5 mM) is thoroughly mixed with alcohol **1a–1f** (5 mM) in a test tube and placed in microwave oven and irradiated for the time specified in the **Table 1**. At the end of exposure to microwaves, the reaction mixture was cooled to room



temperature, monitored on TLC (hexane: EtOAc, 8:2, v/v), the product is extracted into methylene chloride (20 mL). Removal of solvent under reduced pressure and purification on silica gel using 1% EtOAc in hexane afforded the required products **2a–2f** in good yields with high (*E*)-stereoselectivity (**Table 1**).

ACKNOWLEDGMENTS

SR thanks his brothers **SS** and **Dr. SP** for financial support and constant encouragement in research. **SR** also thanks **COSIST** programme in organic synthesis in the School of Chemistry, University of Hyderabad.

REFERENCES

1. Basavaiah, D.; Rao, P.D.; Hyma, R.S. *Tetrahedron* **1996**, *52*, 8001.
2. Basavaiah, D.; Bakthadoss, M.; Pandiaraju, S. *Chem. Commun.* **1998**, 1638.
3. Basavaiah, D.; Pandiaraju, S.; Krishnamacharyulu, M.; Hyma, R.S. *Tetrahedron Lett.* **1997**, *38*, 2141.
4. Caddick, S. *Tetrahedron* **1995**, *51*, 10403.
5. Bram, G.; Loupy, A.; Villemin, D. In *Solid Supports and Catalysts in Organic Chemistry*, Ellis Horwood, London, 1992.
6. Varma, R.S.; Saini, R.K. *Tetrahedron Lett.* **1997**, *38*, 4337.
7. Basavaiah, D.; Krishnamacharyulu, M.; Hyma, R.S.; Sarma, P.K.S. Kumaragurubaran, N. *J. Org. Chem.* **1999**, *64*, 1197.
8. Hoffman, H.M.R.; Rabe, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 795.
9. **Spectral data obtained for 2a:** ¹H NMR (CDCl₃): δ 2.13 (s, 3H), 3.63 & 3.83 (2s, 3H), 6.71 & 7.69 (2s, 1H), 7.19–7.42 (m, 5H). The peak at δ 7.69 was assigned to the olefinic proton of the [*E*]-isomer and a very minor peak at δ 6.71 was assigned to the olefinic proton of the [*Z*]-isomer in very small amounts (6%); ¹³C NMR (CDCl₃): δ 13.72, 127.68, 128.47, 128.73, 129.89, 135.64, 141.21, 174.56; IR (KBr): 1712, 1620 cm⁻¹.

Received in the Netherlands September 14, 2000



Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the [U.S. Copyright Office](#) for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on [Fair Use in the Classroom](#).

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our [Website User Agreement](#) for more details.

[Order now!](#)

Reprints of this article can also be ordered at

<http://www.dekker.com/servlet/product/DOI/101081SCC100104425>