

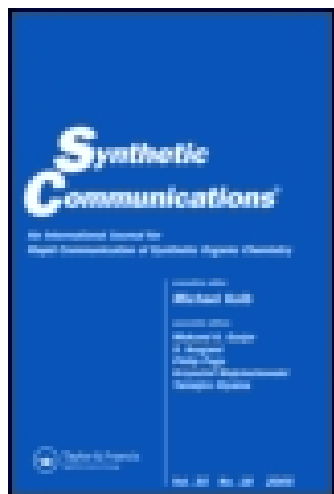
This article was downloaded by: [Tulane University]

On: 07 January 2015, At: 21:34

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/lcyc20>

One Pot Synthesis of α,β -Unsaturated Ketones from the Mukaiyama Aldol Condensation

Ezzeddine Bouhlef^a & Béchir Ben Hassine^a

^a Laboratoire de Synthèse Organique et de Photochimie, Faculté des Sciences, 5000, Monastir, Tunisie

Published online: 24 Sep 2006.

To cite this article: Ezzeddine Bouhlef & Béchir Ben Hassine (1992) One Pot Synthesis of α,β -Unsaturated Ketones from the Mukaiyama Aldol Condensation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 22:15, 2183-2186, DOI: [10.1080/00397919208019070](https://doi.org/10.1080/00397919208019070)

To link to this article: <http://dx.doi.org/10.1080/00397919208019070>

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>

ONE POT SYNTHESIS OF α,β -UNSATURATED
KETONES FROM THE MUKAIYAMA ALDOL
CONDENSATION

Ezzeddine Bouhlel and Béchir Ben Hassine*

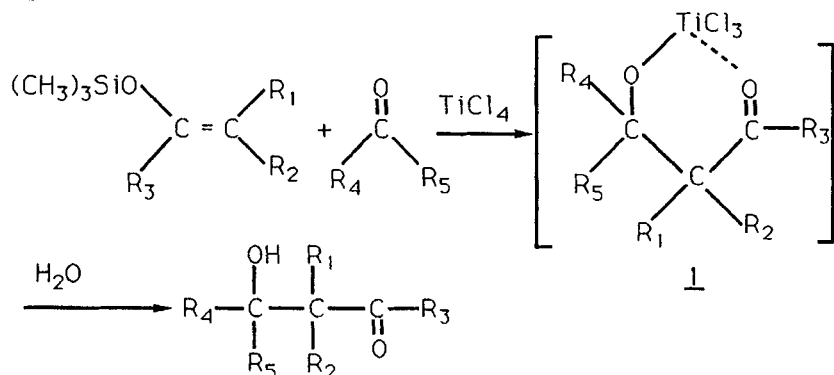
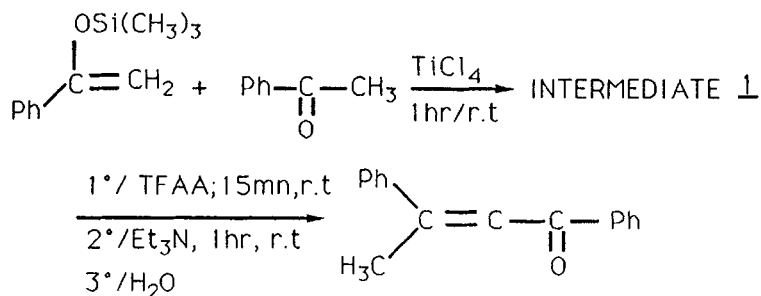
Laboratoire de Synthèse Organique et de Photochimie, Faculté
des Sciences 5000 Monastir, Tunisie.

ABSTRACT

Satisfactory yields of α,β -unsaturated ketones are obtained from two trimethylsilylenol ethers and a variety of aldehydes and ketones in a one pot modified Mukaiyama aldol procedure using triethylamine and trifluoroacetic anhydride.

α,β -Unsaturated ketones are useful intermediates for the production of a large range of compounds. Unfortunately, their synthesis is not always an easy task. They are usually obtained by dehydration of the corresponding β -hydroxyketones, products of aldol condensation. The use of a relatively strong base at elevated temperature as catalyst¹ to effect dehydration and force the aldol condensation to completion is not always successful because the enones can undergo further condensation and lead to polymeric products.

* To whom correspondence should be addressed

Eq.1Eq.2

The Mukaiyama aldol condensation^{2,3} of trimethylsilylenol ethers with aldehydes or ketones in the presence of titanium tetrachloride is well recognised as a standard method for the preparation of cross aldol products, i.e, β -hydroxyketones(eq.1).

We have found that the addition of trifluoroacetic anhydride (TFAA) and triethylamine to the intermediate of the Mukaiyama reaction using the trimethylsilylenol ether of acetophenone with acetophenone affords, after quenching, nearly quantitatively the corresponding α,β -unsaturated ketone (eq.2).

Synthetically useful yields of enones have been obtained using this modified Mukaiyama procedure (see Table)

Table
Synthesis of α,β -unsaturated ketones*

Entry	Silyl enol ether	Carbonyl compound	Enone	%Yield
1				67
2				95
3				57
4				46
5				63
6				56

* All enones were purified by distillation and gave satisfactory spectral and physical properties.

Experimental : typical procedure

A methylene chloride (10ml) solution of 0.961g (5mmol), of 1-phenyl-1-trimethylsilyloxyethane was added dropwise into a mixture of 0.6g (5mmol) of acetaldehyde and 5ml of a 1M TiCl_4 solution in dichloromethane, and the reaction mixture was stirred.

After one hour, 1.05g (5mmol) of trifluoroacetic anhydride (TFAA) was added dropwise and the mixture was stirred for an additional 15min . Triethylamine (1.011g, 10mmol) was added and stirring continued for an additional hour at room temperature . The mixture was quenched with 10ml of a saturated NH_4Cl solution, after wich the organic layer was extracted with ether and the extract concentrated under reduced pressure . The residue was distilled to give 1,3-diphenyl-3-buten-1-one (Bp $246^\circ\text{C}/50\text{mmHg}$) in 95% yield . EI-MS : 222 (M^+ , 19,92) ; 145 (26,36) ; 115 (69,60) ;105(base); 91 (38,32) .

^1H NMR (60MHz) CDCl_3 : δ ppm : 2,52 (d,3H, CH_3) ; 7,07 (m,1H,-C=C-); 7,12-7,60 (m,8H,aromatic); 7,80-8,02 (m,2H,aromatic). IR(neat) : $1560\text{-}1600\text{cm}^{-1}$ (-C=C-); 1650cm^{-1} (-C=O).

Aknowledgment

The authors wish to thank Professor M.W.Rathke of the chemistry departement of Michigan State University for his valuable help and guidance to E.Bouhleh.

REFERENCES :

1. House, H.O., " Modern Synthesis Reactions",W.A.Benjamin, Inc. Philippines, 2nd edition, 1972; pp. 632-659.
2. Mukaiyama, T., Narasaka, K. and Banno, K.,Chem.Letters, 1973,1011.
3. Mukaiyama,T., Banno, K. and Narasaka, K., J.Am.Chem.Soc; 1974,96, 24, 7304.

(Received in UK 30 March, 1992)