This article was downloaded by: [Monash University Library]
On: 06 November 2012, At: 06:42
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

A New Synthesis of 2-Aryl-2-Oxoalkylphosphonates from Triethyl Phosphonoacetate

Dae Young Kim [a], Myeon Sik Kong [a] & Dae Yong Rhie [a]

[a] Department of Chemistry, Soonchunhyang University, Onyang P. O. Box 97 Chungnam, 336-600, Korea

Version of record first published: 16 Feb 2007.

To cite this article: Dae Young Kim, Myeon Sik Kong & Dae Yong Rhie (1995): A New Synthesis of 2-Aryl-2-Oxoalkylphosphonates from Triethyl Phosphonoacetate, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:18, 2865-2869

To link to this article: http://dx.doi.org/10.1080/00397919508011834

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

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.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Monash University Library] at 06:42 06 November 2012

SYNTHETIC COMMUNICATIONS, 25(18), 2865-2869 (1995)

A NEW SYNTHESIS OF 2-ARYL-2-OXOALKYLPHOSPHONATES FROM TRIETHYL PHOSPHONOACETATE

Dae Young Kim,* Myeon Sik Kong and Dae Yong Rhie

Department of Chemistry, Soonchunhyang University, Onyang P. O. Box 97
Chungnam 336-600, Korea

Downloaded by [Monash University Library] at 06:42 06 November 2012

ABSTRACT : Acylation of triethyl phosphonoacetate using magnesium ethoxide affords acyl phosphonoacetates which, on treatment with catalytic *p*-TsOH in water, are converted into 2-aryl-2-oxoalkylphosphonates.

β-Keto phosphonates are valuable intermediates for organic synthesis, especially for the preparation of α,β-unsaturated carbonyl compounds by the Horner-Wadsworth-Emmons condensation.[1] Although a number of syntheses[2] have been developed with goal of providing a route to this class of compounds, they have limitation in terms of the reaction conditions employed, competition

* To whom correspondence should be addressed

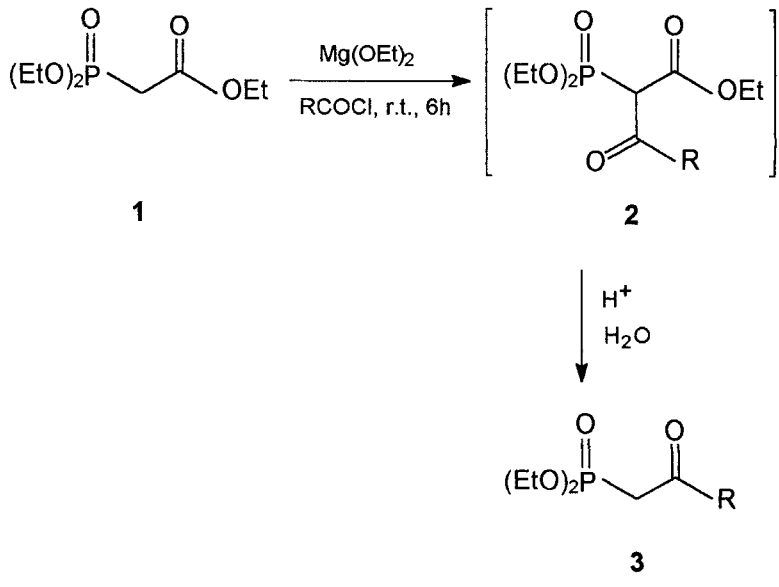
Copyright © 1995 by Marcel Dekker, Inc.

from other reactions. Commonly, β-keto phosphonates are prepared by acylation of alkylphosphonate α-anions with carboxylic acid esters,[3] carboxylic acid chlorides,[4] or N-methoxy-N-methylcarboxamides.[5]

In the continuation of our work on the development of convenient synthetic methods to β-keto phosphonates, we have reported one such route from nitroalkenes to β-keto phosphonates.[6] More recently, we have introduced a convenient route to cyclic β-keto phosphonates from α-nitro epoxides and dialkyl phosphite.[7] In this paper, we wish to report a convenient synthesis of 2-aryl-2-oxoalkylphosphonates **1** from triethyl phosphonoacetate **3**. It was performed by the acylation of trietyl phosphonoacetate **1** using magnesium ethoxide followed by hydrolysis and decarboxylation with catalytic *p*-toluenesulfonic acid in water. By this procedure, 2-aryl-2-oxoalkylphosphonates **3** were prepared in good yields. The results are summarized in Table 1. We found that treatment of aliphatic carboxylic acid chlorides as acylating agent to solution of triethyl phosphonoacetate and magnesium ethoxide affords β-keto phosphonates in low yields.

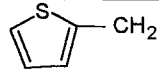
The general experimental procedure is as follows: To a stirred solution of magnesium ethoxide (2.4 mmol) in THF (5 mL) was added triethyl phosphonoacetate (453 mg, 2.0 mmol) at room temperature. After addition, reaction mixture was refluxed for 1h. Carboxylic acid chloride (2.4 mmol) was added dropwise to the reaction mixture at 0^0 C. The reaction mixture was stirred at room temperature for 6h and acidified to pH 1~2 with cold 10 % H_2SO_4 solution, and extracted with ethyl ether. The extract was concentrated *in vacuo*. A solution of *p*-TsOH (10 mg) in water (10 mL) was added to the residue, and then the mixture was refluxed for 4h. After cooling, the mixture

Downloaded by [Monash University Library] at 06:42 06 November 2012



1 2 3

Table 1. Preparation of β–keto phosphonates **3**

R	Yields (%)[a]	R	Yields (%)[a]
Ph	73	3-Br, C_6H_4	71
C_6F_5	98	4-CH_3, C_6H_4	82
4-OCH_3, C_6H_4	85		40
2,5-Cl_2,4-F, C_6H_2	70	Et	26

[a] Isolated yields are based on triethyl phosphonoacetate.

Downloaded by [Monash University Library] at 06:42 06 November 2012

was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as eluent.

Compared with synthetic procedure by the acylation of alkylphosphonates,[3-5] which use strong bases such as n-butyl lithium, this new route to β-keto phosphonates has the advantages of mild reaction conditions and good yields, especially for 2-aryl-2-oxoalkylphosphonates.

Acknowledgement : We thank the Soonchunhyang University for financial support of this research.

References :

1. (a) Wadsworth, W. S. Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961,** 83, 1733. (b) Horner, L.; Hoffmann, H. Klink, W. ;Ertel, H.; Toscano, V. G. *Chem Ber.* **1962,** 95, 581. (c) Wadsworth, W. S. Jr. *Org. React. (N. Y.),* **1977**, 25, 73. (d) Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983,** 24, 4405. (e) Blanchette, M. A.; Choy, W.; Davis, J. T.; Essenfeld, A. P.; Masamune, S.; Roush, W. R.; Sakai, T. *Tetrahedron Lett.* **1984,** 25, 2183. (f) Mashall, J. A.; DeHoff, B. S.; Cleary, D. G. *J. Org. Chem.* **1986,** 51, 1735. (g) Koskinen, A. M. P.; Koskinen, P. M. *Synlett* **1993,** 501. (h) Paterson, I.; Yeung, K.; Smaill, J. B. *Synlett* **1993,** 774.

2. (a) Lichtenthaler, F. W. *Chem. Rev.* **1961**, 61, 607. (b) Honda, M.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1984,** 25, 3857. (c) Herzig, C.; Gasteiger, J. *Chem. Ber.* **1982,** 115, 601. (d) Lee, K.; Wiemer, D. F.

Downloaded by [Monash University Library] at 06:42 06 November 2012

J. Org. Chem. **1991,** 56, 5, 556. (e) Calogeropoulou, T.; Hammond, G. B.; Wiemer, D. F. *J. Org. Chem.* **1987,** 52, 4185. (f) Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. *J. Am. Chem. Soc.* **1981,** 103, 1224. (g) Crobel, B.; Medinger, L.; Haelters, J. P.; Sturtz, G. *Synthesis* **1985**, 1048. (h) Boeckman, R. K. Jr.; Walters, M. A.; Koyano, H. *Tetrahedron Lett.* **1989,** 30, 4787. (i) Kabat, M. M. *Tetrahedron Lett.* **1993**, 34, 8543. (j) Ruder, S. M.; Kulkarni, V. R. *Synthesis* **1993**, 945. (k) Delamarche, I.; Mosset, P. *J. Org. Chem.* **1994,** 59, 5453. (l) Narkunam, K.; Nagarajan, M. *J. Org. Chem.* **1994,** 59, 6386. (m) Kim, D. Y.; Mang, J. Y.; Oh, D. Y. *Synth. Commun.* **1994,** 24, 629.

3. (a) Corey, E. J.; Kwiatkowski, G. T. *J. Am. Chem. Soc.* **1966,** 88, 5654. (b) Coutrout, P.; Savignac, P.; Mathay, F. *Synthesis* **1978,** 36. (c) Aboujaoude, E. E.; Colligan, N.; Savignac, P. *J. Organomet. Chem.* **1984,** 264, 9. (d) Rudisill, D. E.; Whitten, J. P. *Synthesis* **1994,** 851.
4. (a) Hong, S.; Chang, K.; Ku, B.; Oh, D. Y. *Tetrahedron Lett.* **1989**, 30, 3307. (b) Mathey, F.; Savignac, P. *Synthesis* **1976,** 766. (c) Savignac, P.; Mathey, F. *Tetrahedron Lett.* **1976**, 2829.; (d) Mathey, F.; Savignac, P.; *Tetrahedron* **1978,** 649.
5. Theisen, P. D.; Heathcock, C. H. *J. Org. Chem.* **1988,** 53, 2374.
6. (a) Kim, D. Y.; Lee, K.; Oh, D. Y. *J. Chem. Soc. Perkin Trans. 1,* **1992,** 2451. (b) Kim, D. Y.; Mang, J. Y.; Lee, J. W.; Oh, D. Y. *Bull. Korean Chem. Soc.* **1993,** 14, 526.
7. Kim, D. Y.; Kong, M. S. *J. Chem. Soc. Perkin Trans. 1,* **1994,** 3359.

(Received in the UK 31 January 1995)

Downloaded by [Monash University Library] at 06:42 06 November 2012