Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1578-1580

NOTE

Stereoselective Conversion of Dialkyl-2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)butanedioates to Dialkyl-(*Z*)-2-(2-Acetylphenoxy)-2-butenedioates

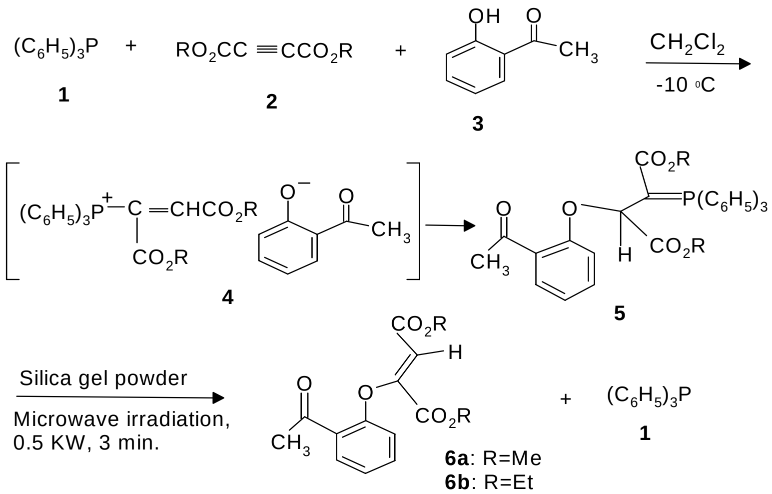
ALI RAMAZANI*, MAHSHID RAHIMIFARD, ALI SOULDOZI, ABBAS AZIZIAN,
MAHSA KARDAN, NADER NOSHIRANZADEH and ASIEH SAFARI
Chemistry Department, Zanjan University, P.O. Box 45195-313, Zanjan, Iran
E-mail: aliramazani@gmail.com

Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 1-(2-hydroxyphenyl)-1-ethanone leads to vinyltriphenylphosphonium salts, which undergo Michael addition reaction with conjugate base to produce dialkyl 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)-butanedioates. Silica gel powder was found to catalyze stereoselective conversion of dialkyl 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)butanedioates to dialkyl-(*Z*)-2-(2-acetylphenoxy)-2-butenedioates in solvent-free conditions under microwave irradiation at microwave power 0.5 KW in 3 min.

Key Words: 1-(2-Hydroxyphenyl)-1-ethanone, Silica gel, Michael addition, Acetylenic esters, Vinyltriphenylphosphonium salt, Microwave irradiation.

β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis[1-3]. Organophosphorus compounds have been extensively used in organic synthesis[2]. Silica gel as an additive promotes the Wittig reactions of phosphorus ylides with aldehydes, including sterically hindered aldehydes to increase the rate and yields of alkenes[4,5]. In the past, a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts has been reported[1,3]. In this article, the catalytic role of silica gel powder in the stereoselective conversion of dialkyl-2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)butanedioates (**5**) to dialkyl-(*Z*)-2-(2-acetylphenoxy)-2-butenedioates (**6**) in solvent-free conditions[6] under microwave irradiation at microwave power 0.5 KW in 3 min is reported (**Scheme-1**).

IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively.



Scheme-1

General procedure for the preparation of ylides 5 and compounds 6a-b: To a magnetically stirred solution of triphenylphosphine (**1**) (1 mmol) and 1-(2-hydroxyphenyl)-1-ethanone (**3**) (1 mmol) in CH_2Cl_2 (4 mL) was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (3 mL) at -10ºC over 15 min. The mixture was allowed to warm up to room temperature. Silica gel powder (1.5 g) was added and the solvent was evaporated. Dry silica gel and the residue were irradiated for 3 min at microwave power 0.5 KW and then placed over a column of silica gel powder (12 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:10) as eluent. The solvent was removed under reduced pressure and products were obtained as colourless viscous oils (**6a**: Yield; 19%. **6b**: Yield: 14%.). The characterization data of the compounds (**6a-b**) are given in our previous report[7].

The ylide **5** may result from initial addition of triphenylphosphine (**1**) to the acetylenic ester (**2**) and concomitant protonation of the 1:1 adduct by 1-(2-hydroxyphenyl)-1-ethanone leads to vinyltriphenylphosphonium salts (**4**) which undergo Michael addition reaction with conjugate base to produce dialkyl 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)-butanedioates (**5**). TLC indicated formation of ylides **5** in CH_2Cl_2. Silica gel powder was found to catalyze stereoselective conversion of dialkyl-2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)butanedioates (**5**) to dialkyl-(*Z*)-2-(2-acetylphenoxy)-2-butenedioates (**6**) in solvent-free conditions[6] under microwave irradiation at microwave power 0.5 KW (**Scheme-1**). TLC indicated that the reaction was completed after 3 min.

In summary, the silica gel powder is able to catalyze stereoselective conversion of ylides **5** to compounds **6** in solvent-free conditions[6] under microwave irradiation at microwave power 0.5 KW in 3 min. (**Scheme-1**). Other aspects of this process are under investigation.

ACKNOWLEDGEMENT

This work was supported by the Sandoogh Hemayate as Pajuoheshgharane Keshvare, Iran *via* the research project number N 84114.

REFERENCES

1. A. Ramazani, L. Yousefi, E. Ahmadi and A. Souldozi, *Phosphorus, Sulfur Silicon Rel. Elem.*, **179**, 1459 (2004) and references cited therein.
2. J.I.G. Cadogan, Organophosphorus Reagents in Organic Synthesis, Academic Press, New York (1979).
3. A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41**, 567 (2000).
4. V. J. Patil and U. Mavers, *Tetrahedron Lett.*, **37**, 1281 (1996).
5. C. Xu, G. Chen, C. Fu and X. Huang, *Synth. Commun.*, **25**, 2229 (1995).
6. K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000).
7. A. Ramazani, M. Rahimifard and A. Souldozi, *Asian J. Chem.*, **18**, 695 (2006).

(*Received*: 11 October 2005; *Accepted*: 20 September 2006) AJC-5135