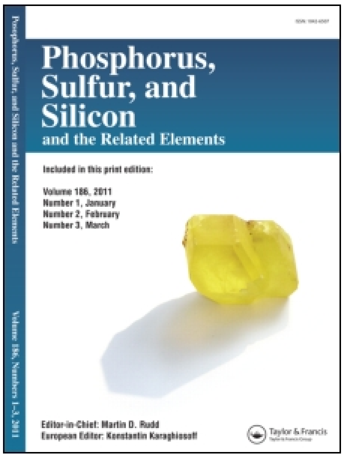


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

MICROWAVE INDUCED SYNTHESIS OF COUMARINS FROM IN SITU GENERATED STABILIZED PHOSPHORUS YLIDES IN THE PRESENCE OF SILICA GEL POWDER IN SOLVENT-FREE CONDITIONS

Ali Ramazani[a]; Ali Souldozi[a]
[a] Zanjan University, Zanjan, Iran

To cite this Article Ramazani, Ali and Souldozi, Ali(2004) 'MICROWAVE INDUCED SYNTHESIS OF COUMARINS FROM IN SITU GENERATED STABILIZED PHOSPHORUS YLIDES IN THE PRESENCE OF SILICA GEL POWDER IN SOLVENT-FREE CONDITIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 3, 529 — 533
To link to this Article: DOI: 10.1080/10426500490422173
URL: http://dx.doi.org/10.1080/10426500490422173

Phosphorus, Sulfur, and Silicon, 179:529–533, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490422173

MICROWAVE INDUCED SYNTHESIS OF COUMARINS FROM IN SITU GENERATED STABILIZED PHOSPHORUS YLIDES IN THE PRESENCE OF SILICA GEL POWDER IN SOLVENT-FREE CONDITIONS

Ali Ramazani and Ali Souldozi
Zanjan University, Zanjan, Iran

(Received September 2, 2003)

Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by phenols (1-hydroxynaphthalene, 2-hydroxynaphthalene and 4-bromophenol) leads to vinyltriphenylphosphonium salts, which undergo aromatic electrophilic substitution reaction with conjugate base to produce corresponding stabilized phosphorus ylides. Microwave was found to catalyze conversion of the stabilized phosphorus ylides to corresponding coumarins in the presence of silica gel powder in solvent-free conditions.

Keywords: Coumarin; microwave; phenol; silica gel; solvent-free conditions

Coumarins are very well known natural products and many such compounds exhibited high levels of biological activity.[1] Coumarins also are used as additives to food and cosmetics,[2] optical brightening agents,[3] and dispersed flurescent and laser dyes.[4] In addition some coumarins are of much interest because of their toxcicity,[5] carcinogenity,[6] and photodynamic effects.[7] 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.[8] In the absence of suitable catalysts, Wittig reaction of the stabilized phosphorus ylides are very slow.[9] Remarkable rate enhancements and dramatic reductions of reaction times in the Wittig reactions were observed[9] when a mixture of triphenylcarbethoxymethylene phosphorane, an aldehyde

---

This work was supported by the Zanjan University.

Address correspondence to Ali Ramazani, Chemistry Department, Zanjan University, PO Box 45195-313, Zanjan, Iran. E-mail: a-ramazani@mail.znu.ac.ir

and silica gel was irradiated in a microwave oven for 5–6 min. In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[10–14] Recently we reported on the catalytic role of silica gel powder in the synthesis of coumarins in solvent-free conditions[15] in fairly good yields.[16] The use of microwave irradiation to bring about organic transformations has taken new dimensions in recent years.[17] In this article, we report on the catalytic role of microwave in conversion of in situ generated stabilized phosphorus ylides (**5**) to corresponding coumarins (**6**) in the presence of silica gel powder in solvent-free conditions (Scheme 1).

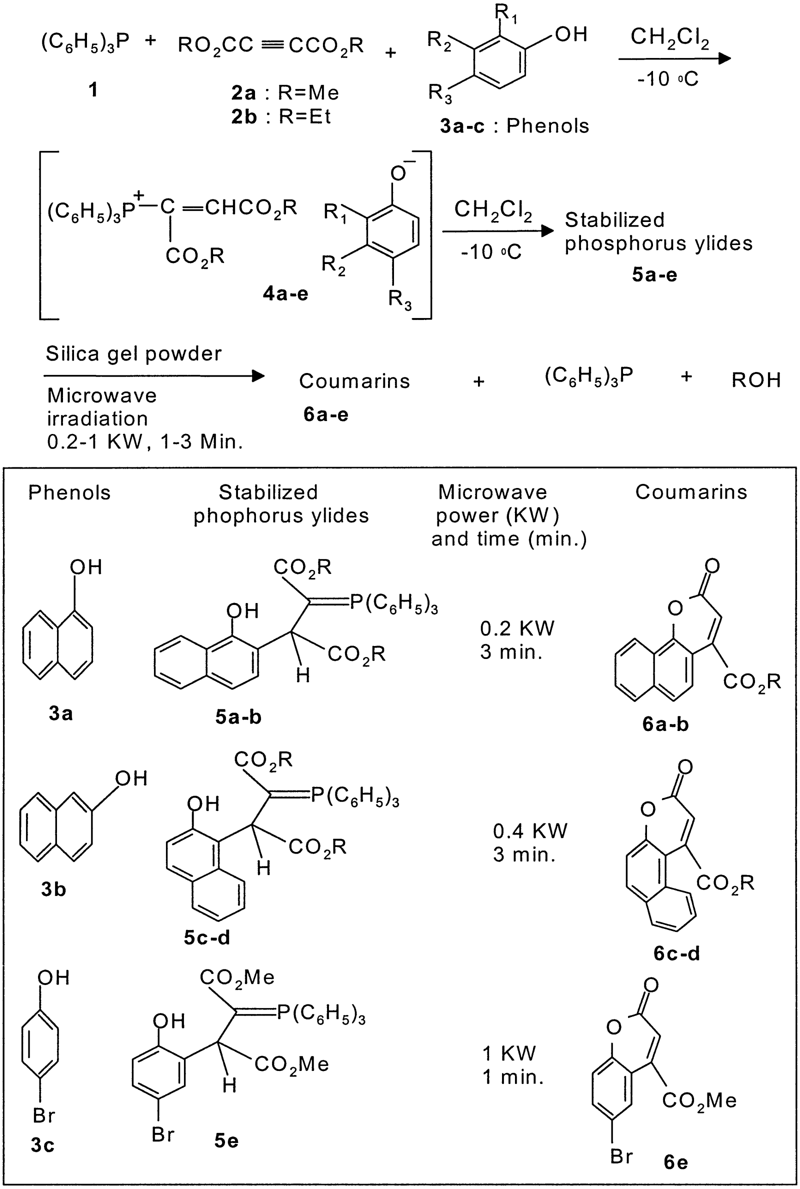
RESULTS AND DISCUSSION

The stabilized phosphorus ylide (**5**) may result from initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by the electrophilic attack of the vinyltriphenylphosphonium cation to the aromatic ring at *ortho* position relative to the strong activating group (Scheme 1). TLC indicated formation of ylides **5** in CH_2Cl_2. Microwave irradiation was found to catalyze conversion of ylides **5** to corresponding coumarins (**6a–e**) in the presence of silica gel powder in solvent-free conditions (Scheme 1). TLC indicated that the reactions were completed in the solid phase (silica gel powder) under microwave irradiation at microwave power 0.2–1 KW after 1–3 min. The structures **6a–e** were deduced from their melting points, IR and ^{1}H NMR spectra. All of these data are the same as our previous reports data for the compounds **6a–e**.[16,18,19]

In summary, we have found that microwave irradiation is able to catalyze conversion of in situ generated stabilized phosphorus ylides (**5**) to corresponding coumarins (**6**) in the presence of silica gel powder in solvent-free conditions (Scheme 1). Other aspects of this process are under investigation.

EXPERIMENTAL

Commerical oven butane M245 was used for microwave irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. UV spectra were recorded on a Shimadzu UV-2100 spectrophothometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER


(C6H5)3P + RO2CC≡CCO2R + 3a-c : Phenols
1
2a : R=Me
2b : R=Et
R1
R2
R3
OH
CH2Cl2
-10 °C
(C6H5)3P+—C=CHCO2R
CO2R
O−
4a-e
CH2Cl2
-10 °C
Stabilized phosphorus ylides
5a-e
Silica gel powder
Microwave irradiation
0.2-1 KW, 1-3 Min.
Coumarins
6a-e
+ (C6H5)3P + ROH
Phenols
Stabilized phophorus ylides
Microwave power (KW) and time (min.)
Coumarins
3a
5a-b
0.2 KW
3 min.
6a-b
3b
5c-d
0.4 KW
3 min.
6c-d
3c
5e
1 KW
1 min.
6e
P(C6H5)3
CO2R
CO2Me
Br
H

SCHEME 1

DRX-500 AVANCE spectrometer at 500 and 125 MHz respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

General Procedure for the Preparation of Coumarins (6a–e)

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and phenol **3** (1 mmol) in CH_2Cl_2 (5 ml) was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (3 ml) at –10°C over 15 min. The mixture was allowed to warm up to room temperature. Silica gel powder (2 g) was added and the solvent was evaporated. Dry silica gel and the residue were irradiated in the microwave oven at microwave power 0.2–1 KW (20–100%) for 1–3 min (see Scheme 1) and then placed over a column of silica gel (10 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 orange crystals (**6a–b**), reddish crystals (**6c–d**) and white crystals (**6e**). The characterization data of the compounds (**6a–e**) are given in our previous reports.[16,18,19]

Methyl 2-Oxo-2H-benzo[h]chromene-4-carboxylate (6a)

Orange crystals, m.p. 162.2–162.3°C; yield: 84%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 376, 3.544; 324, 3.791; 276, 4.166; 226, 4.403. IR (KBr) (ν_{max}, cm^{-1}): 3032, 2951, 1762, 1241. MS(m/z, %): 254 (M^+, 100), 226(100); 225(100); 194(100); 167(60); 137(100); 89(20).

Ethyl 2-Oxo-2H-benzo[h]chromene-4-carboxylate (6b)

Orange crystals, m.p. 145.2–145.5°C; yield: 82%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 356, 3.944; 323, 3.857; 254, 3.986; 230, 4.427. IR (KBr) (ν_{max}, cm^{-1}): 3048, 2967, 1725, 1258. MS(m/z, %): 268 (M^+, 100), 239(100); 195(100); 167(90); 139(100); 137(50); 89(10).

Methyl 3-Oxo-3H-benzo[f]chromene-1-carboxylate (6c)

Reddish crystals, m.p. 138.2–138.8°C; yield: 56%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 368, 3.684; 325, 3.608; 258, 3.734; 227, 4.102. IR (KBr) (ν_{max}, cm^{-1}): 3048, 2983, 1725, 1258. MS(m/z, %): 254 (M^+, 100), 226(100); 225(70); 194(100); 139(90); 138(100).

Ethyl 3-Oxo-3H-benzo[f]chromene-1-carboxylate (6d)

Reddish crystals, m.p. 135.9–136.4°C; yield: 60%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 356, 3.944; 323, 3.857; 254, 3.987; 230, 4.428. IR (KBr)

($\nu_{\max}$, cm^{-1}): 3032, 2952, 1733, 1258. MS(m/z, %): 268 (M$^+$, 100), 266(70); 239(100); 222(40); 212(90); 193(100); 168(80); 140(80); 138(100).

Methyl 6-Bromo-2-oxo-2H-chromene-4-carboxylate (6e)

White crystals, m.p. 115.7–115.9°C; yield: 71.5%. UV (EtOH 95%) ($\lambda_{\max/\mathrm{nm}}$, log ε): 345, 4.029; 286, 4.363; 223, 4.786; 210, 4.789. IR (KBr) ($\nu_{\max}$, Cm^{-1}): 3032, 2975, 1709, 1241. MS(*m*/*z*, %): 284 (M$^+$+2, 70), 281 (M$^+$, 100), 254 (20), 226(80); 223(95); 192(30); 178(22); 167(17); 148 (10).

REFERENCES

[1] R. D. H. Muvay, J. Mendey, and S. A. Brown, *The Natural Coumarins* (Wiley, New York, 1982).
[2] R. O. Kenedy and R. D. Tharnes, *Coumarins: Biology, Application and Mode of Action* (Wiley, Chichester, 1997).
[3] M. Zahradink, *The Production and Application of Flurescent Brightening Agents* (Wiley, 1992).
[4] M. Maeda, *Laser Dyes* (Academic Press, New York, 1994).
[5] S. Kadis, A. Ciegler, and S. Ajl, *Meorev*, **7,** 1 (1972).
[6] G. P. Ellis and G. B. West, *Plwg. Med. Chem.*, **10,** 109 (1974).
[7] P. Wells and H. Mossison, *J. Am. Chem. Soc.*, **97,** 154 (1975).
[8] V. J. Patil and U. Mavers, *Tetrahedron Lett.*, **37,** 1281 (1996).
[9] C. Xu, G. Chen, C. Fu, and X. Huang, *Synth. Commun.*, **25,** 2229 **(**1995**)**.
[10] A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41,** 567 (2000).
[11] I. Yavari and A. Ramazani, *Synth. Commun.*, **27,** 1385 (1997).
[12] I. Yavari, A. Ramazani, and A. Yahya-Zadeh, *Synth. Commun.*, **26,** 4495 (1996).
[13] I. Yavari and A. Ramazani, *Phosphorus, Sulphur, and Silicon*, **130,** 73 (1997).
[14] A. Ramazani, N. Shajari, and F. Gouranlou, *Phosphorus, Sulphur, and Silicon*, **174,** 223 (2001).
[15] K. Tanaka and F. Toda, *Chem. Rev.*, **100,** 1025 (2000).
[16] A. Ramazani and A. Souldozi, *Phosphorus, Sulphur, and Silicon*, **178,** 1325 (2003).
[17] S. Munavalli, D. K. Rohrbaugh, G. W. Wagner, F. R. Longo, and H. D. Durst, *Phosphorus, Sulphur, and Silicon*, **177,** 781 (2002).
[18] A. Ramazani and A. Souldozi, *Phosphorus, Sulphur, and Silicon*, **178,** 1329 (2003).
[19] A. Ramazani and A. Souldozi, *Phosphorus, Sulphur, and Silicon*, **178,** 0000 (2003).