Asian Journal of Chemistry Vol. 18, No. 1 (2006), 120-124

Kaolinite Powder as an Efficient Catalyst for the Preparation of Coumarins from *in Situ* Generated Stabilized Phosphorus Ylides in Solvent-free Conditions

ALI RAMAZANI*, ISSA AMINI†‡ and ABDOLHOSSAIN MASSOUDI‡
Chemistry Department, Zanjan University
P.O. Box 45195-313, Zanjan, Iran
E-mail: a-ramazani@mail.znu.ac.ir; aliramazani@yahoo.com

Protonation of the highly reactive 1 : 1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylene-dicarboxylates, by phenols (1-hydroxynaphthalene and 2-hydroxy-naphthalene) leads to vinyltriphenylphosphonium salts, which undergo aromatic electrophilic substitution reaction with conjugate base to produce corresponding stabilized phosphorus ylides. Kaolinite powder was found to catalyze conversion of the stabilized phosphorus ylides to coumarins in solvent-free conditions at 80–90°C in 1 h in fairly high yields. Microwave also was found to catalyze the same reactions in the presence of kaolinite powder in solvent-free conditions at microwave power 0.18–0.45 kW in 3 min.

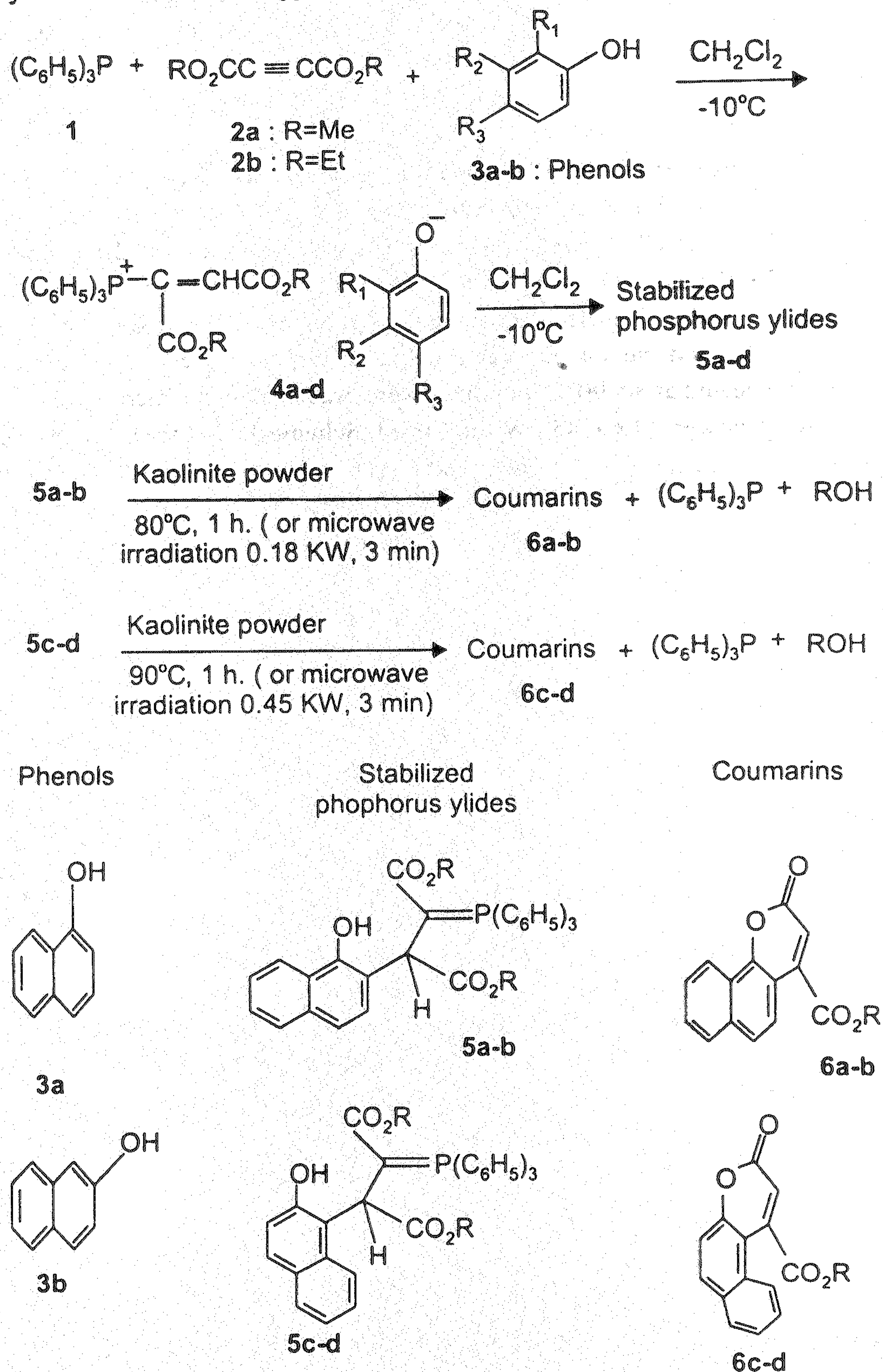
Key Words: Kaolinite, Solvent-free conditions, Microwave, Phenol, Coumarin, Stabilized phosphorus ylides.

INTRODUCTION

Coumarins are used as additives to food and cosmetics[1, 2], optical brightening agents[3] and dispersed fluorescent and laser dyes[4]. In addition, some coumarins are of much interest as a result of their toxicity[5], carcinogenity[6], and photodynamic effects[7]. In the past, a convenient one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts was established[8]. The use of microwave irradiation to bring about organic transformations has taken new dimensions in the recent years[9, 10]. In this paper, the catalytic role of kaolinite ($Al_2(OH)_4Si_2O_5$) powder in conversion of in situ generated stabilized phosphorus ylides (**5**) to corresponding coumarins (**6**) in solvent-free conditions[9, 10] under thermal and microwave conditions is reported

†Chemistry Department, Peyam Noor University of Abhar, P.O. Box 97, Abhar, Iran.
‡Chemistry Department, Peyam Noor University of Mashhad, P.O. Box 91735-433, Mashhad, Iran.

(**Scheme-1**). Kaolinite ($Al_2(OH)_4Si_2O_5$) is an inexpensive easily available mineral clay that has found wide applications in industrial processes[11].



Scheme-1

EXPERIMENTAL

Commercial oven Butane M245 was used for microwave irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. 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.

General procedure for the preparation of coumarins (6a–d): 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. Thermally activated dry kaolinite ($Al_2(OH)_4Si_2O_5$) powder (2 g) was added and the solvent was evaporated. Dry kaolinite powder and the residue were heated at 80–90°C for 1 h (or were irradiated in the microwave oven at microwave power 0.18–0.45 kW for 1 min) (**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 (**6a**: m.p. 162°C, yield 82%; **6b**: m.p. 145°C, yield 80%; **6c**: m.p. 138°C, yield 55%; **6d**: m.p. 136°C, yield 60%) as orange crystals (**6a–b**) and light green crystals (**6c–d**).

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. Kaolinite ($Al_2(OH)_4Si_2O_5$) powder was found to catalyze conversion of the stabilized phosphorus ylides (**5a–d**) to coumarins (**6a–d**) in solvent-free conditions at 80–90°C in 1 h in fairly high yields. Microwave also was found to catalyze the same reactions in the presence of kaolinite powder in solvent-free conditions at microwave power 0.18–0.45 kW in 3 min (**Scheme-1**). The structures of **6a–d** were deduced from their melting points, IR, ^{1}H NMR and ^{13}C NMR spectra and also *via* X-ray single crystal structure determination (for **6c**) (Figs. 1 and 2)[12]. All of these data are the same as previously reported data for the compounds **6a–d**[12, 13].

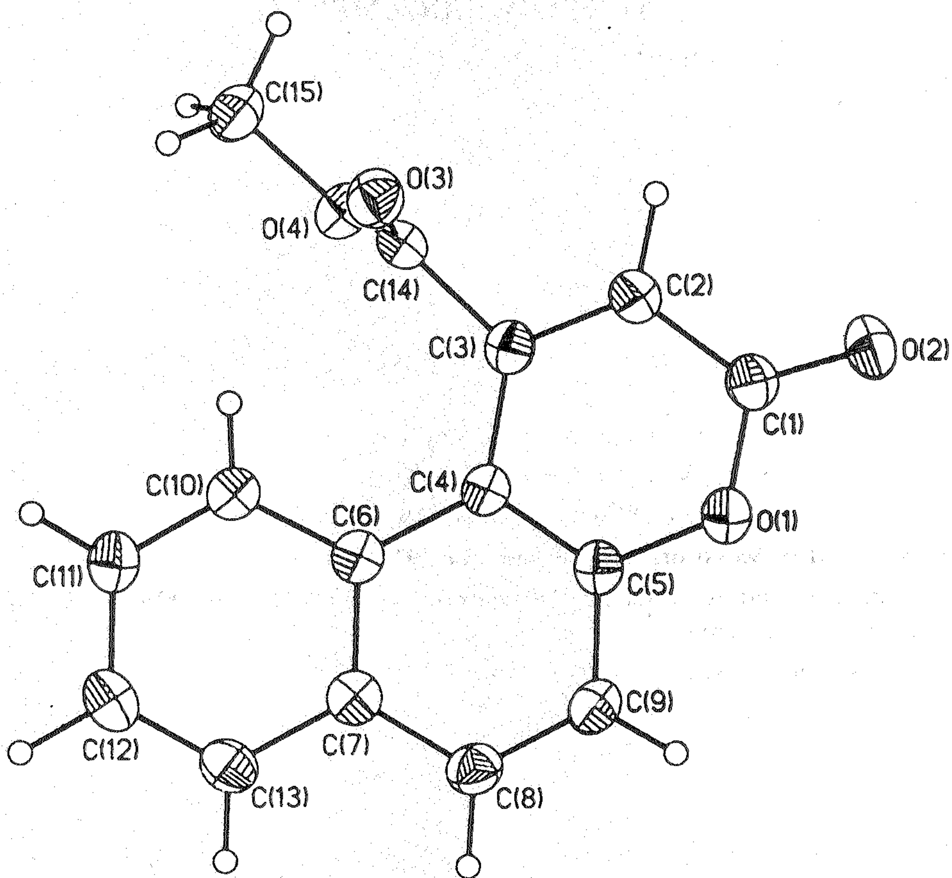


Fig. 1. Molecular structure of **6c**.

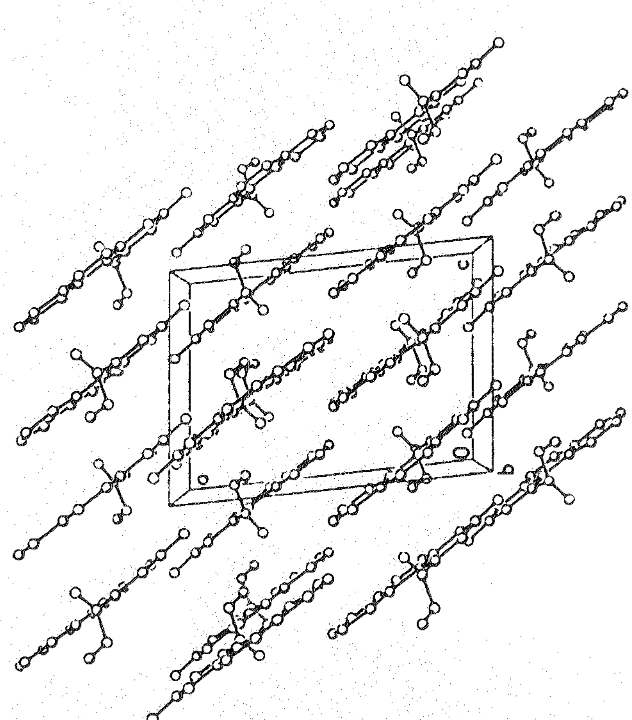


Fig. 2. Unit cell crystal structure of **6c**.

ACKNOWLEDGEMENTS

This work was supported by the Peyam Noor Universities of Abhar and Mashhad, Iran.

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 Fluorescent 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. A. Ramazani and A. Bodaghi, *Phosphorus, Sulfur and Silicon*, **179**, 1615 (2004) and references cited therein.
9. K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000).
10. S. Munavalli, D.K. Rohrbaugh, G.W. Wagner, F.R. Longo and H.D. Durst, *Phosphorus, Sulphur and Silicon*, **177**, 781 (2002).
11. N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, New York (1985).
12. A. Ramazani, A. Morsali, N. Noshiranzadeh, B. Mohammadi, A. Souldozi, F. Jamali and F. Gouranlou, *Z. Kristallogr., NCS*, **217**, 393 (2002).
13. A. Ramazani and A. Souldozi, *Phosphorus, Sulphur and Silicon*, **178**, 1325, 1329 (2003).

(*Received*: 8 October 2004; *Accepted*: 5 September 2005) AJC-4372