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NOTE

Bentonite Powder Catalyzed Synthesis of Coumarins from *in situ* Generated Stabilized Phosphorus Ylides in Solvent-free Conditions

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Protonation of the highly reactive 1 : 1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by phenols (1-hydroxynaphthalene and 2-hydroxynaphthalene) leads to vinyltriphenylphosphonium salts, which undergo aromatic electrophilic substitution reaction with conjugate base to produce corresponding stabilized phosphorus ylides. Bentonite powder was found to catalyze the 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 bentonite powder in solvent-free conditions at microwave power 0.18–0.45 KW in 3 min.

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

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 toxcicity[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 bentonite 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 **(Scheme-1)**. Bentonite is an inexpensive easily available mineral clay that has found wide applications in industrial process[11].

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. ^1H 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

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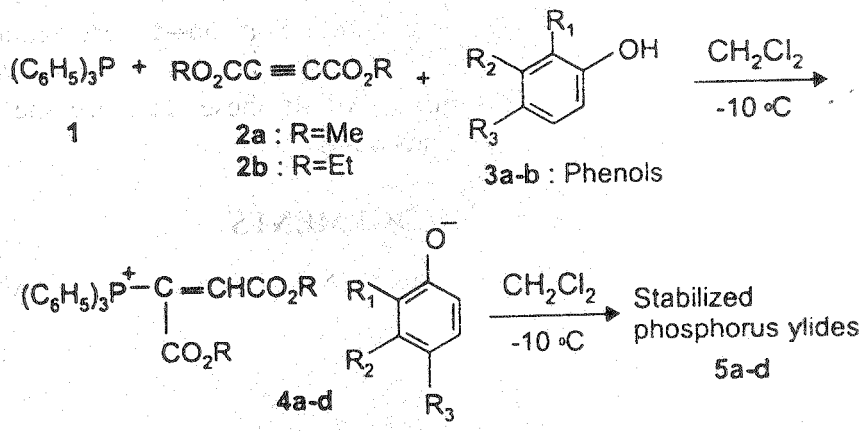
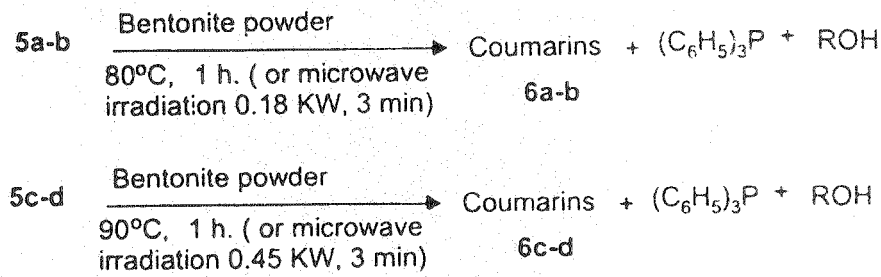
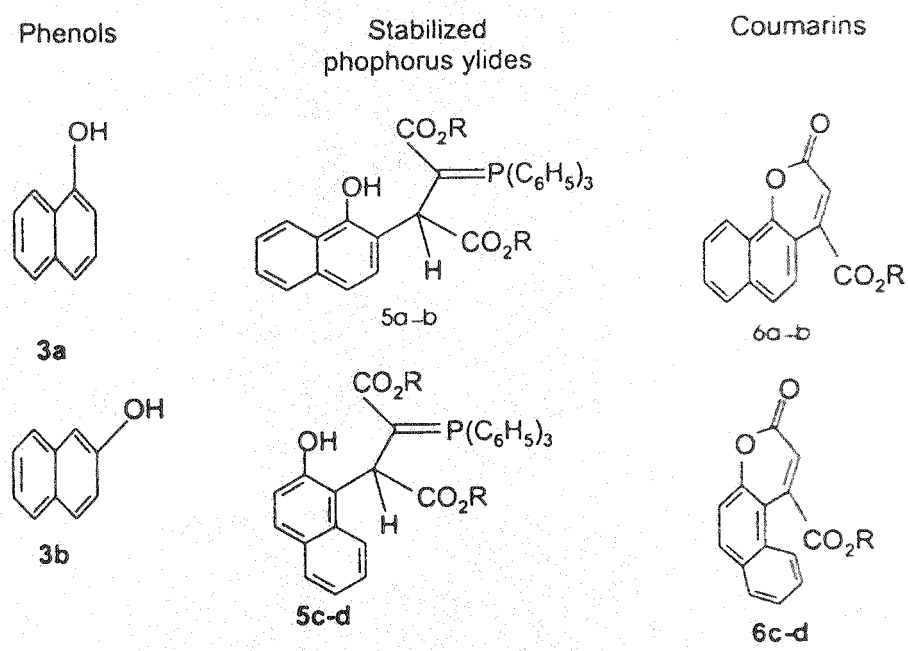
CH_2Cl_2 (3 mL) at –10°C over 15 min. The mixture was allowed to warm up to room temperature. Thermally activated dry bentonite powder (2 g) was added and the solvent was evaporated. Dry bentonite powder and the residue were heated at 80–90°C for 1 h (or were irradiated in the microwave oven at microwave 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 end products were obtained.







Scheme-1

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. Bentonite 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 bentonite 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**)[12]. All of these data are the same as previously reported data for the compounds **6a–d**[12–14].

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