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Synthesis of Coumarins from *in situ* Generated Stabilized Phosphorus Ylides in the Presence of Solid Catalysts 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. Iron(II) sulfate powder was found to catalyze conversion of the stabilized phosphorus ylides to coumarins in solvent-free conditions at 90°C in 1 h in high conversions. Microwave also was found to catalyze the same reactions in the presence of iron(II) sulfate powder in solvent-free conditions at microwave power 1 kW in 1 min. Na_2SO_4, $NaHSO_4$ and $CuSO_4$ powders are not able to catalyze the reaction. $ZnSO_4$ powder is able to catalyze the reaction (only in the cases of 2-hydroxynaphthalene).

Key Words: Iron(II) sulfate, Solvent-free conditions, Microwave, Phenol, Coumarin, Zinc sulfate.

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 toxcicity[5], carcinogenicity[6], and photodynamic effects[7]. In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts[8–12]. Recently we have reported on catalytic role of silica gel powder in the synthesis of coumarins in solvent-free conditions in fairly good yields[13]. The use of microwave irradiation to bring about organic transformations has taken new dimensions in recent years[14, 15]. In this paper, we report on the catalytic role of iron(II) sulfate powder and zinc sulfate powder in conversion of

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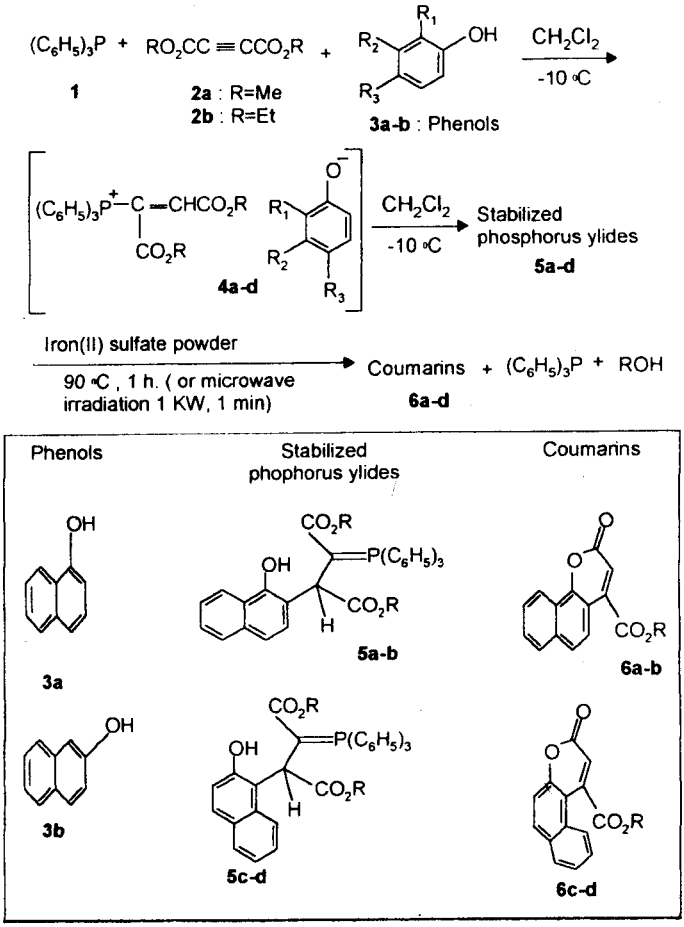
in situ generated stabilized phosphorus ylides (**5**) to corresponding coumarins (**6**) in solvent-free conditions under thermal and microwave conditions (**Scheme 1**).



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. Iron(II) sulfate powder was found to catalyze conversion of the stabilized phosphorus ylides (**5c–d**) to coumarins (**6c–d**) in solvent-free conditions at 90°C in 1 h in high conversions. (In this condition, ylides **5a–b** are stable and no products were observed.) Microwave was found to catalyze conversion of the stabilized phosphorus ylides (**5a–d**) to coumarins (**6a–d**) in the presence of iron(II) sulfate

powder in solvent-free conditions at microwave power 1 kW in 1 min. We have also used Na_2SO_4, $NaHSO_4$ $CuSO_4$ and $ZnSO_4$ powders instead of iron(II) sulfate powder in this reaction; only $ZnSO_4$ powder was found to catalyze conversion of the stabilized phosphorus ylides **(5c–d)** to coumarins **(6c–d)** in solvent-free conditions. In the other cases the corresponding product **6** was not observed. The structures **6a–d** were deduced from their melting points, IR and ^1H NMR spectra and also *via* X-ray single crystal structure determination (Fig. 1) (for **6c**)[18]. All of these data are the same as our previous reports data for the compounds **6a–d**[13, 16–18].

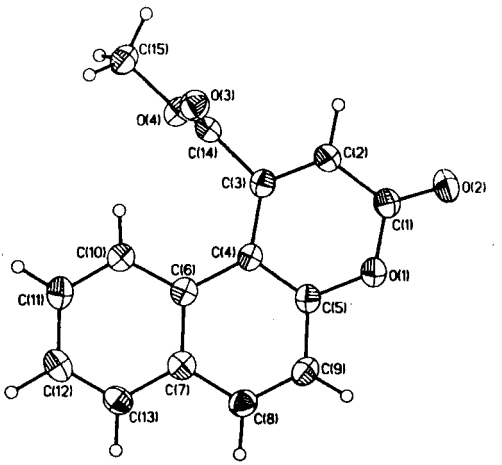


Fig. 1. ORTEP drawing of **6c**

EXPERIMENTAL

Commerical 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 CH_2Cl_2 (3 mL) at –10°C over 15 min. The mixture was allowed to warm up to room temperature. Iron(II) sulfate powder (2 g) was added and the solvent was evaporated. Dry iron(II) sulfate powder and the residue were heated for 1 h at 90°C (or were irradiated in the microwave oven at microwave power 1 kW (100%) for 1 min.) 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 (yields: 60–65%) as orange crystals **(6a–b)** and reddish crystals **(6c–d)**.

The characterization data of the compounds **(6a–d)** are given in our previous reports[16, 18, 19].

In summary, we have found that iron(II) sulfate powder is able to catalyze conversion of *in situ* generated stabilized phosphorus ylides **5** to corresponding coumarins **6** in solvent-free conditions under thermal and microwave conditions **(Scheme-1).** We also have found that zinc sulfate powder is able to catalyze conversion of ylides **5c–d** to corresponding coumarins **6c–d.** Other aspects of this process are under investigation.

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