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Synthesis of Electron-Poor Coumarins from *in situ* Generated Stabilized Phosphorus Ylides in the Presence of Talc Powder in Solvent-free Conditions and Investigation of their Photochemical Reactions

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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. Talc powder was found to catalyze conversion of the stabilized phosphorus ylides to coumarins in solvent-free conditions at 80-90ºC in 1 h in fairly high yields. Microwave was also found to catalyze the same reactions in the presence of talc powder in solvent-free conditions at microwave power 0.18-0.45 KW in 3 min. Photochemical reactions of the electron-poor coumarins were investigated.

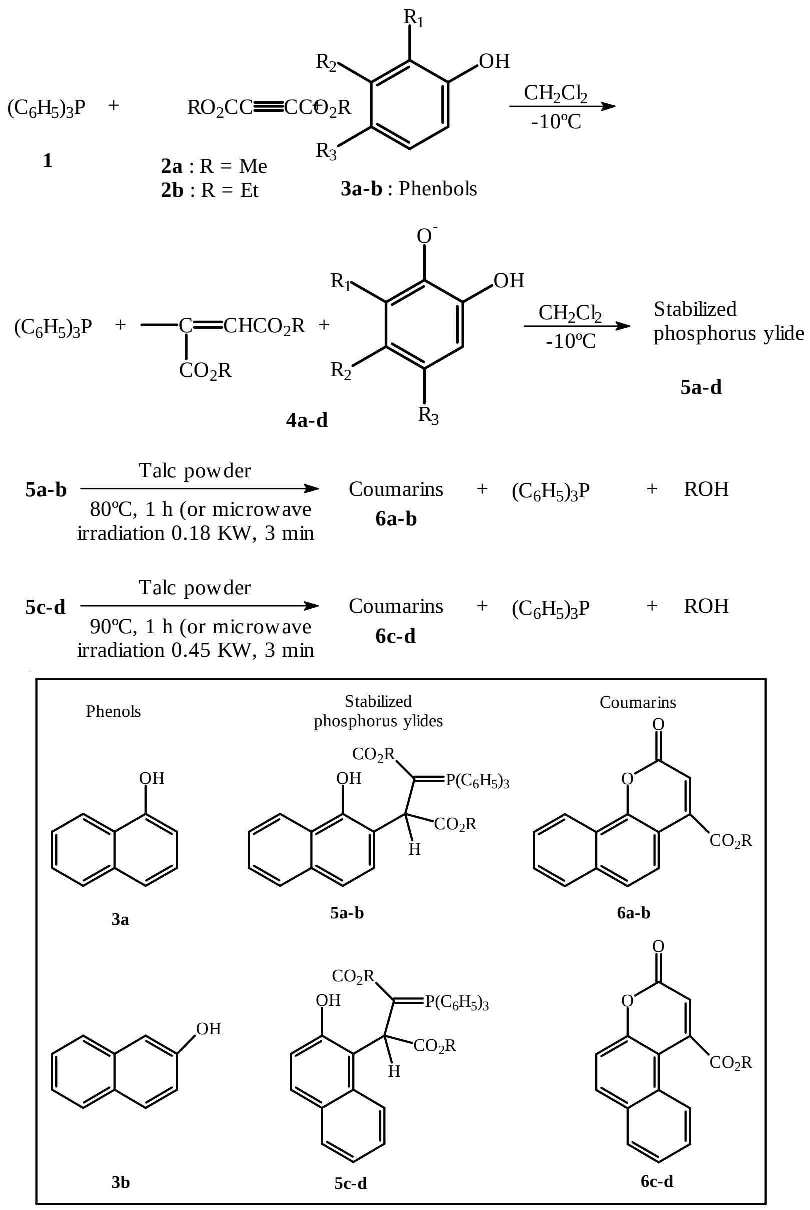
Key Words: Talc, Solvent-free conditions, Microwave, Phenol, Electron-poor coumarin, Stabilized phosphorus ylides, Photochemical reactions.

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], carcinogenity[6] and photodynamic effects[7]. The author has already reported a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts[8]. The use of microwave irradiation to bring about organic transformations has taken new dimensions in the recent years[9,10]. In this work, the catalytic role of talc 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**). Talc is an inexpensive easily available mineral clay, which have wide applications in industrial process[11].

EXPERIMENTAL

Commerical oven Butane M 245 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.



Scheme-1

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 solution 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. Thermally activated dry bentonite powder (2 g) was added and the solvent was evaporated. Dry talc powder and the residue were heated at 80-90ºC 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. The characterization data of the compounds **6a-d** are given in our previous reports[12-14].

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 vinyltriphenyl-phosphonium 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. Talc powder was found to catalyze conversion

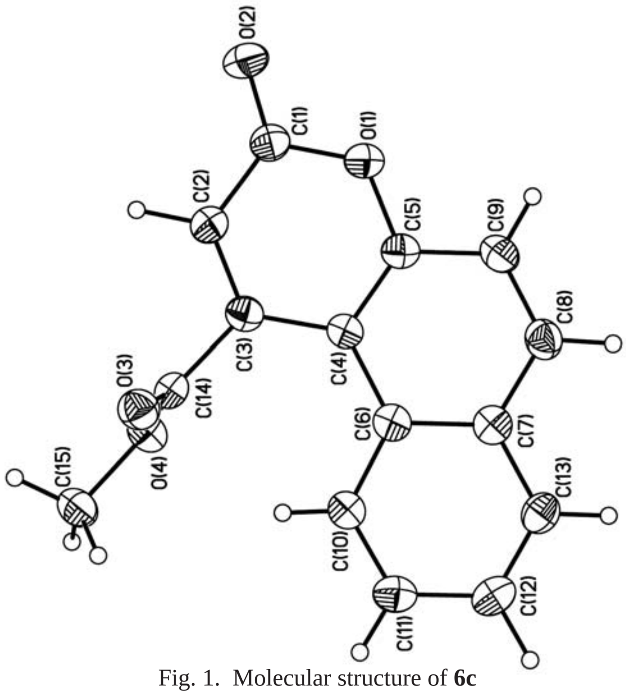


Fig. 1. Molecular structure of **6c**

of the stabilized phosphorus ylides **5a-d** to coumarins **6a-d** in solvent-free conditions at 80-90ºC in 1 h in fairly high yields. Microwave was also found to catalyze the same reactions in the presence of talc powder in solvent-free conditions at microwave power 0.18-0.45 KW in 3 min (**Scheme-1**). Photochemical reactions of the electron-poor coumarins were investigated under sunlight. In the case of **6a** two photochemical compounds were observed. Single crystals of one of them were prepared. 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 (**6c**)[12] (Fig. 1). All of these data are the same as our previous reports data for the compounds **6a-d**[12-14].

Conclusion

It is suggested that talc 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**). Photochemical reactions of the electron-poor coumarins were investigated. Other aspects of this process are under investigation.

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