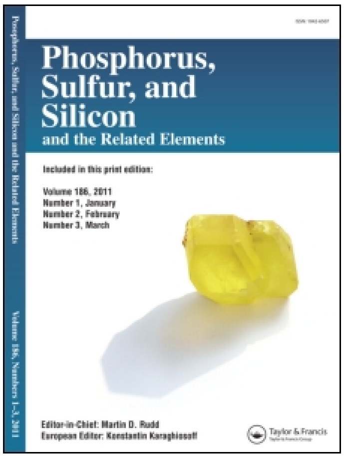

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CONVERSION OF IN SITU GENERATED STABILIZED PHOSPHORUS YLIDES TO CHROMENE DERIVATIVES IN SOLVENT-FREE CONDITIONS

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CONVERSION OF IN SITU GENERATED STABILIZED PHOSPHORUS YLIDES TO CHROMENE DERIVATIVES 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, 2-hydroxynaphthalene, 4-bromophenol, 2-hydroxybenzaldehyde, and 5-bromo-2-hydroxybenzaldehyde) leads to vinyltriphenylphosphonium salts, which undergo electrophilic substitution reaction with conjugate base to produce corresponding stabilized phosphorus ylides. Microwave was found to catalyze conversion of the stabilized phosphorus ylides to chromene derivatives in the presence of solid catalysts in solvent-free conditions at microwave power 0.4 KW in 3 min.

Keywords: Chromene; coumarin; dipotassium hydrogen phosphate; microwave; phenol; silica gel; solvent-free conditions

Chromene skeleton compounds are very well known natural products and many such compounds exhibited high levels of biological activity.[1] Chromene skeleton compounds are also used as additives to food and cosmetics,[2] optical brightening agents,[3] and dispersed flurescent and laser dyes.[4] In addition some chromene skeleton compounds are of much interest as a result of their toxcicity,[5] carcinogenity,[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 the catalytic rule of silica gel powder in the synthesis of coumarins in solvent-free conditions[13] in fairly good yields.[14] The use of microwave irradiation to bring about organic transformations has taken new dimensions in

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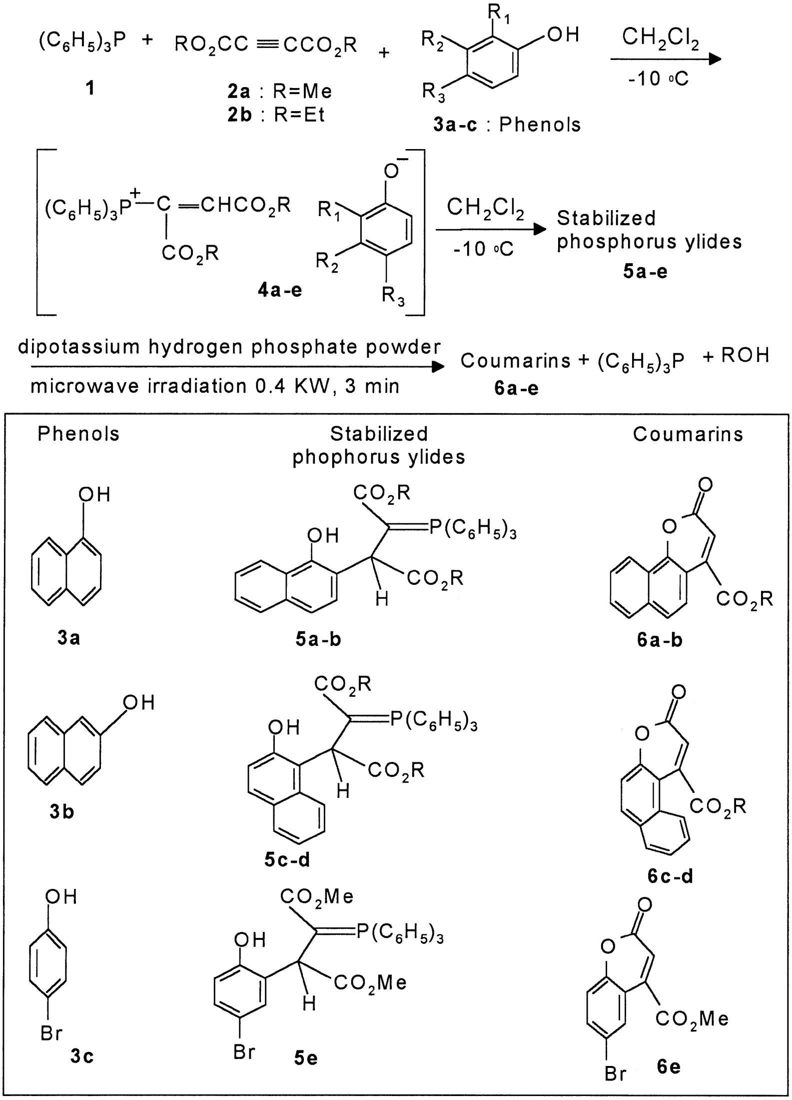
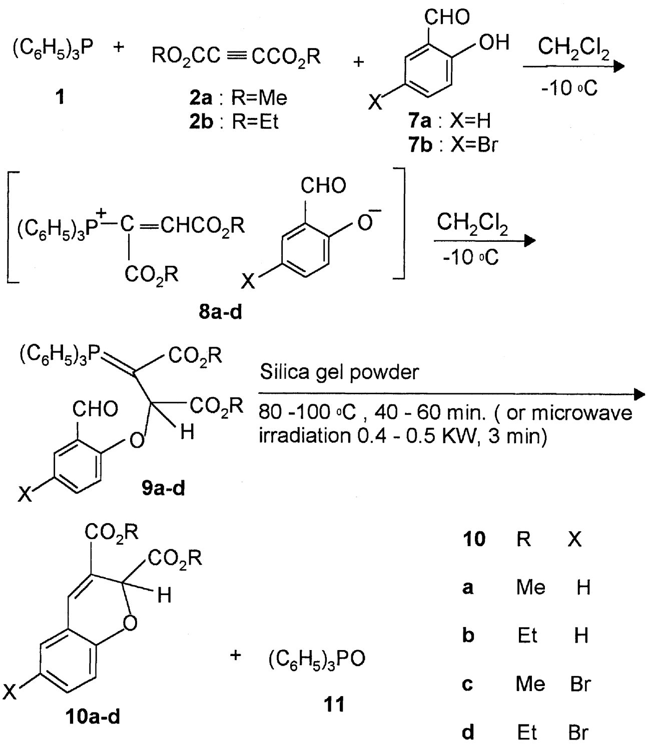
the recent years.[15] In this article, we report on the catalytic rule of dipotassium hydrogen phosphate and silica gel powder in conversion of in situ generated stabilized phosphorus ylides (**5**, **9**) to corresponding oxygen containing heterocyclic compounds (**6**, **10**) in solvent-free conditions under thermal and microwave conditions (Schemes 1 and 2).



SCHEME 1



10	R	X
a	Me	H
b	Et	H
c	Me	Br
d	Et	Br

SCHEME 2

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 was found to catalyze conversion of the stabilized phosphorus ylides (**5**) to coumarins (**6a–e**) in the presence of dipotassium hydrogen phosphate powder in solvent-free conditions at microwave power 0.4 KW in 3 min. The reaction proceeds smoothly and cleanly under solvent-free conditions and no side reactions were observed. In the absence of dipotassium hydrogen phosphate powder under thermal conditions (20–90°C), this reaction did not afford the corresponding compounds (**6a–d**) and in some cases, decomposition of the ylides **5a–d** were observed, but surprisingly catalytic rule of dipotassium hydrogen phosphate powder was observed in conversion of ylide **5e** to **6e** in solvent-free conditions at room temperature in 15 min. We have also used K_3PO_4 and KH_2PO_4 in this reaction under thermal and microwave conditions but in all cases the products were not observed, and in some cases decomposition of the ylides **5a–e** were observed.

The structures **6a–e** were deduced from their melting points, IR and ^{1}H NMR spectra and also via x-ray single crystal (for **6c**) structure determination.[21] All of these data are the same as our previously reported data for the compounds **6a–e**.[14,16,17,21]

We have also used 2-hydroxybenzaldehyde (**7a**) and 5-bromo-2-hydroxybenzaldehyde (**7b**) in this reaction (Scheme 2).

Silica gel powder was found to catalyze formation of chromene derivatives (**10a–d**) from in situ generated stabilized phosphorus ylides (**9a–d**)[12] under thermal and microwave heating in solvent-free conditions[13] with high conversions (Scheme 2).[10–13] TLC indicated that the reaction was completed after 40–60 min at 80–100°C under thermal conditions. The reaction was completed after 3 min under microwave irradiation at microwave power 0.4–0.5 KW. The reaction proceeds smoothly and cleanly under solvent-free conditions[13] (in all cases the reaction works efficiently with high conversions) and no side reactions were observed. In the absence of silica gel powder, this reaction was completed after 24 h in CH_2Cl_2 at room temperature.[19,20] The structures **10a–d** were deduced from their ^{1}H NMR, and ^{13}C NMR spectra and also via x-ray single crystal (for **10c**) structure determination.[18] The characterization data of the compounds (**10a–d**) are given in our previous reports.[18–20]

In summary, we have found that dipotassium hydrogen phosphate powder is able to catalyze conversion of in situ generated stabilized phosphorus ylides (**5**) to corresponding coumarins (**6**) in solvent-free conditions under microwave irradiation (Scheme 1). We have also found that silica gel powder is able to catalyze conversion of ylides **9**[19,20] to compounds **10**[19,20] and triphenylphosphine oxide **11** in solvent-free conditions (Scheme 2). 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. 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–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. Dipotassium hydrogen phosphate powder (2 g) was added and the solvent was evaporated. Dry dipotassium hydrogen phosphate powder and the residue were irradiated in the microwave oven at microwave power 0.4 KW (40%) for 3 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 the products were obtained as orange crystals (**6a** (67%) and **6b** (83%)), reddish crystals (**6c** (62%) and **6d** (27%)), and white crystals (**6e** (72%)) (see Scheme 1). The characterization data of the compounds (**6a–e**) are given in our previous reports.[14,16,17]

General Procedure for the Preparation of Chromenes (10a–d)

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and phenol **7** (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 heated at 80–100°C for 40–60 min (for **10a**: 80°C, 40 min; **10b**: 80°C, 45 min; **10c**: 100°C, 60 min; **10d**: 100°C, 60 min). The reaction was also completed after 3 min under microwave irradiation at microwave power 0.4–0.5 KW (for **10a**: 0.4 KW, 3 min; **10b**: 0.4 KW, 3 min; **10c**: 0.5 KW, 3 min; **10d**: 0.5 KW, 3 min) (see Scheme 2). The characterization data of the compounds (**10a–d**) are given in our previous reports.[18–20]

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