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NOTE

Microwave Induced Synthesis of Alkyl-2-(2-alkoxy-2-(oxoethyl)dinaphtho[2,1-d:1,2-f][1,3]-dioxepin-2-carboxylates from Stabilized Phosphorus Ylides

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 1,1-binaphthyl-2,2'-diol leads to vinyltriphenylphosphonium salts, which undergo Michael addition reaction with conjugate base to produce corresponding stabilized phosphorus ylides. Magnesium oxide powder was found to catalyze conversion of the stabilized phosphorus ylides to alkyl 2-(2-alkoxy-2-oxoethyl)dinaphtho[2,1-d:1,2-f][1,3]-dioxepin-2-carboxylates in solvent-free conditions under microwave (0.6 KW, 3 min) and thermal (100ºC, 1 h) conditions.

Key Words: Magnesium oxide, 1,1-Binaphthyl-2,2'-diol, Michael addition, Vinyltriphenylphosphonium salt, Microwave irradiation, Acetylenic esters.

β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a convenient and synthetically useful method in organic synthesis[1-3]. Silica gel as an additive promotes the Wittig reactions of phosphorus ylides with aldehydes, including sterically hindered aldehydes to increase the rate and yields of alkenes[4,5]. Earlier, a convenient, one-pot method is established for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts[1,3]. In this paper, the catalytic role of magnesium oxide powder in the conversion of stabilized phosphorus ylides to alkyl 2-(2-alkoxy-2-oxoethyl)dinaphtho[2,1-d:1,2-f][1,3]-dioxepin-2-carboxylates in solvent-free conditions under microwave (0.6 KW, 3 min) and thermal (100ºC, 1 h) conditions is reported (**Scheme-1**).

Commercial oven butane M245 was used for microwave irradiation. 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.

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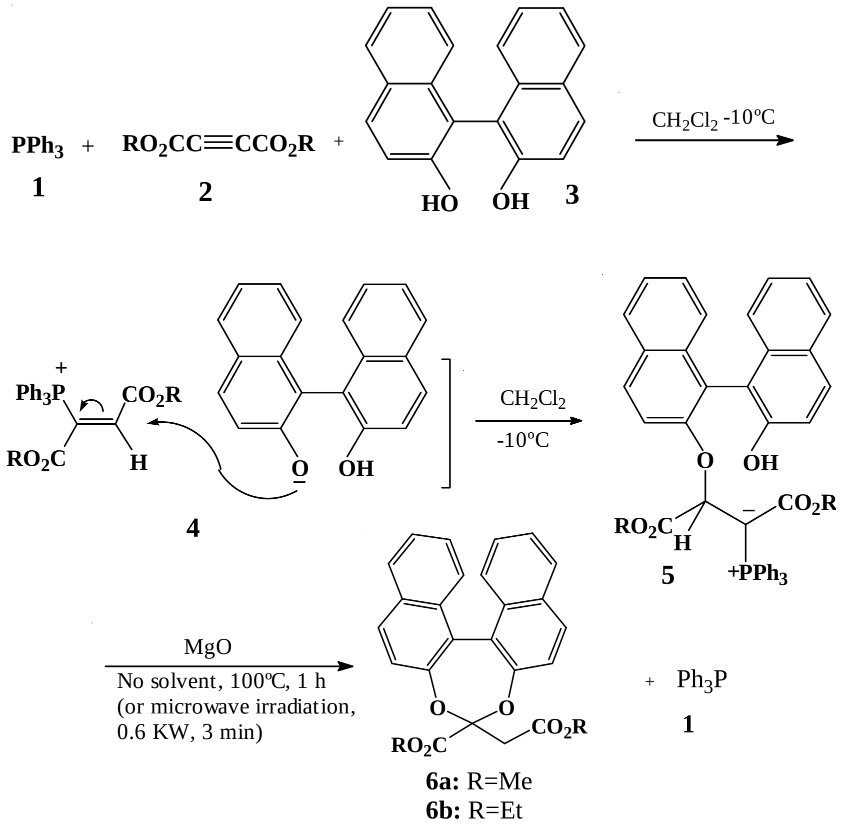

Scheme-1

General procedure for the preparation of ylides 5 and compounds 6a-b: To a magnetically stirred solution of triphenylphosphine (**1**) (1 mmol) and 1,1-binaphthyl-2,2'-diol (**3**) (1 mmol) in CH_2Cl_2 (4 mL) was added dropwise a mixture 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. Magnesium oxide (1.5 g) was added and the solvent was evaporated. Dry magnesium oxide and the residue were heated for 1 h at 100ºC (or irradiated in microwave oven for 3 min at microwave power 0.6 KW) and then placed over a column of silica gel powder (12 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 as yellow crystals (**6a-b**) (**Scheme-1**). The characterization data of the compounds (**6a-b**) are given previously[6].

The ylide **5** may result from initial addition of triphenylphosphine (**1**) to the acetylenic ester (**2**) and concomitant protonation of the 1:1 adduct by 1,1-binaphthyl-2,2'-diol (**3**) leads to vinyltriphenylphosphonium salts (**4**) which undergo Michael addition reaction with conjugate base to produce stabilized phosphorus ylide **5**. TLC indicated formation of ylides **5** in CH_2Cl_2. Magnesium oxide powder was found to catalyze conversion of the stabilized phosphorus ylide **5** to alkyl 2-(2-alkoxy-2-oxoethyl)dinaphtho-[2,1-d:1,2-f][1,3]-dioxepin-2-carboxylates (**6**) in solvent-free conditions under microwave (0.6 KW, 3 min) and thermal (100ºC, 1 h) conditions (**Scheme-1**). We have also used Al_2O_3 in this reaction, but the yield of product was very low and decomposition and several products also were observed.

In conclusion, the magnesium oxide powder is found to catalyze conversion of the ylides **5** to compounds **6** in solvent-free conditions6 (**Scheme-1**). Other aspects of this process are under investigation.

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