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NOTE

Stereoselective Synthesis of Dialkyl-1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-dicarboxylates

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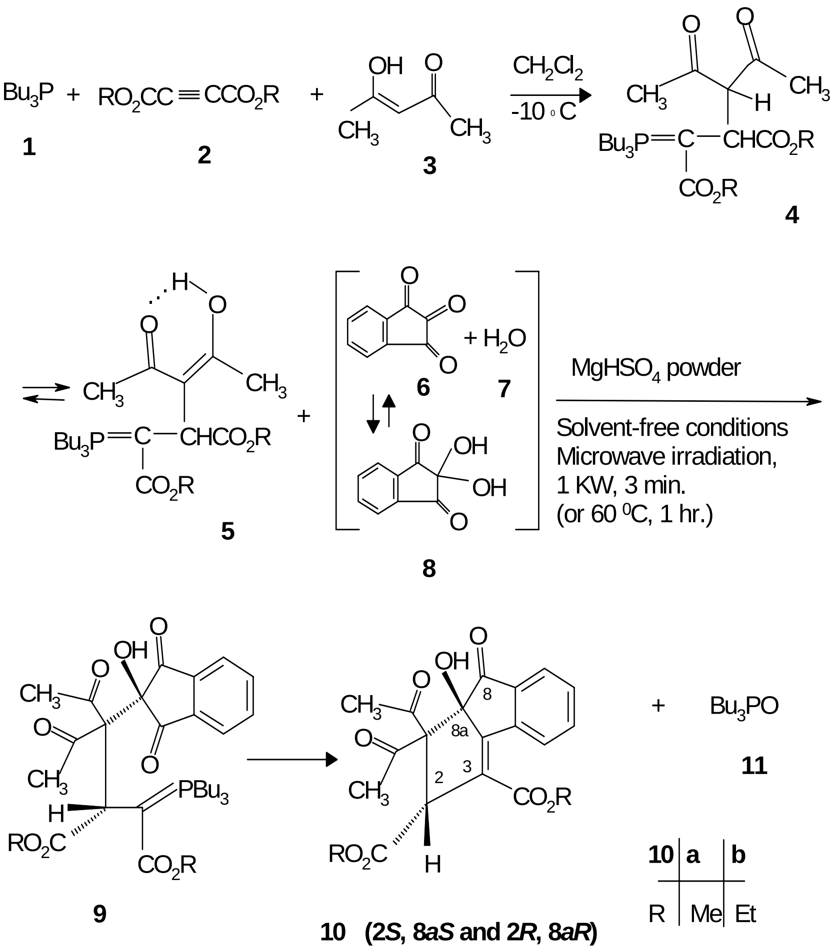
Protonation of the highly reactive 1:1 intermediates produced in the reaction between tributylphosphine and dialkyl acetylenedicarboxylates by acetylacetone leads to sterically congested phosphorus ylides. Reaction between the sterically congested phosphorus ylides with ninhydrin leads to stereoselective synthesis of dialkyl 1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-carboxylates in the presence of magnesium hydrogen sulfate powder in solvent-free conditions under microwave (1 KW, 3 min) and thermal (60ºC, 60 min) conditions.

Key Words: Magnesium hydrogen sulfate, Wittig reaction, Solvent-free conditions, Ninhydrin, Tributylphosphine, Microwave irradiation.

Organophosphorus compounds have been extensively used in organic synthesis[1,2]. A well known method for achieving alkenylation is the Wittig reaction[1]. In the past, one-pot method for preparing of stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts has been established[1]. In present communication, a facial one-pot stereoselective synthesis of dialkyl-1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-dicarboxylates (**10**) by the reaction of dialkyl-2-(1-acetyl-2-oxopropyl)-3-(tributylphosphoranylidene)succinates (**4**) and indene-1,2,3-trione (**6**) (**Scheme-1**) in the presence of magnesium hydrogen sulfate powder in solvent-free conditions under microwave (1 KW, 3 min) and thermal (60ºC, 1 h) conditions is reported.

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C NMR spectra were measured with a Bruker DRX-500 AVANCE spectrometer at 500, 125 and 470.6 MHz, respectively.



Scheme-1

General procedure for the preparation of dialkyl-1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-dicarboxylates (10a-b): To a magnetically stirred solution of tributylphosphine (**1**) (1 mmol) and acetylacetone (**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 and the solvent was removed under reduced pressure. The homogeneous mixture of the dried residue (ylide **4**), magnesium hydrogen sulfate powder (2 g) and powdered indane-1,2,3-trione (1 mmol, **6**, prepared from powdered ninhydrin (**8**) under thermal conditions (4 h at 120ºC) in oven) were irradiated for 3 min at microwave power 1 KW (or heated in oven at 60ºC for 1 h) and then mixture placed over a column of silica gel (12 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:9) as eluent.

The solvent was removed under reduced pressure and products were obtained as white crystals (**6a-b**). The characterization data of dialkyl-1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-dicarboxylates (**10a-b**) are given in our previous report[3].

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from a phosphorane and a carbonyl compound such as an aldehyde or ketone[4]. Thus, compounds **10** may be regarded as the product of an intramolecular Wittig reaction. Such addition-olefination products may result from an initial addition of tributylphosphine (**1**) to the acetylenic ester (**2**) and concomitant protonation of the 1:1 adduct, followed by attack of the acetylacetone anion on the vinylphosphonium cation[5] to form phosphorane (**4**). Attack of the stabilized ylide **5** on the highly electron deficient carbonyl group of indane-1,2,3-trione (**6**), would lead to the stabilized ylide **9**. Intramolecular Wittig reaction of stabilized ylide **9** leads to dialkyl-1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]-indene-2,3-dicarboxylates (**10**) and tributylphosphine oxide (**11**) in the presence of magnesium hydrogen sulfate powder in solvent-free conditions under microwave (1 KW, 3 min) and thermal (60ºC, 1 h) conditions (**Scheme-1**). We have proved the stereochemistry of compound **10a** (2R, 8aR and its mirror image 2S, 8aS) *via* single crystal X-ray diffraction method[3,6].

In summary, we have developed a new and convenient, one-pot stereoselective method for preparing dialkyl 1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-dicarboxylates (**10**) utilizing *in situ* generation of the phosphorane **4**. Other aspects of this process are under investigation.

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