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NOTE

Silica Gel Powder Catalyzed Stereoselective Synthesis of Dialkyl 1,1-Diacetyl-8*a*-hydroy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-dicarboxylates from the Reaction of Dialkyl 2-(1-Acetyl-2-oxopropyl)-3-(tributylphosphoranylidene)succinates with Ninhydrin in Solvent-free Conditions

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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. Silica gel powder was found to catalyze intermolecular reaction of the sterically congested phosphorus ylides with indene-1,2,3-trione in solvent-free system under thermal and microwave conditions.

Key Words: Microwave, Tributylphosphine, Acetylenic esters, Intramolecular wittig reaction, Ninhydrin, Silica gel.

Organophosphorus compounds have been extensively used in organic synthesis[1,2]. A well known method for achieving alkenylation is the Wittig reaction[1]. 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 very convenient and synthetically useful method in organic synthesis[1,2]. In the past we have established a convenient, one-pot method for preparation of stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts[1]. In present work, a facial stereoselective synthesis of dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-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**) in the presence of silica gel powder in solvent-free system under thermal and microwave conditions has been reported (**Scheme-1**).

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.

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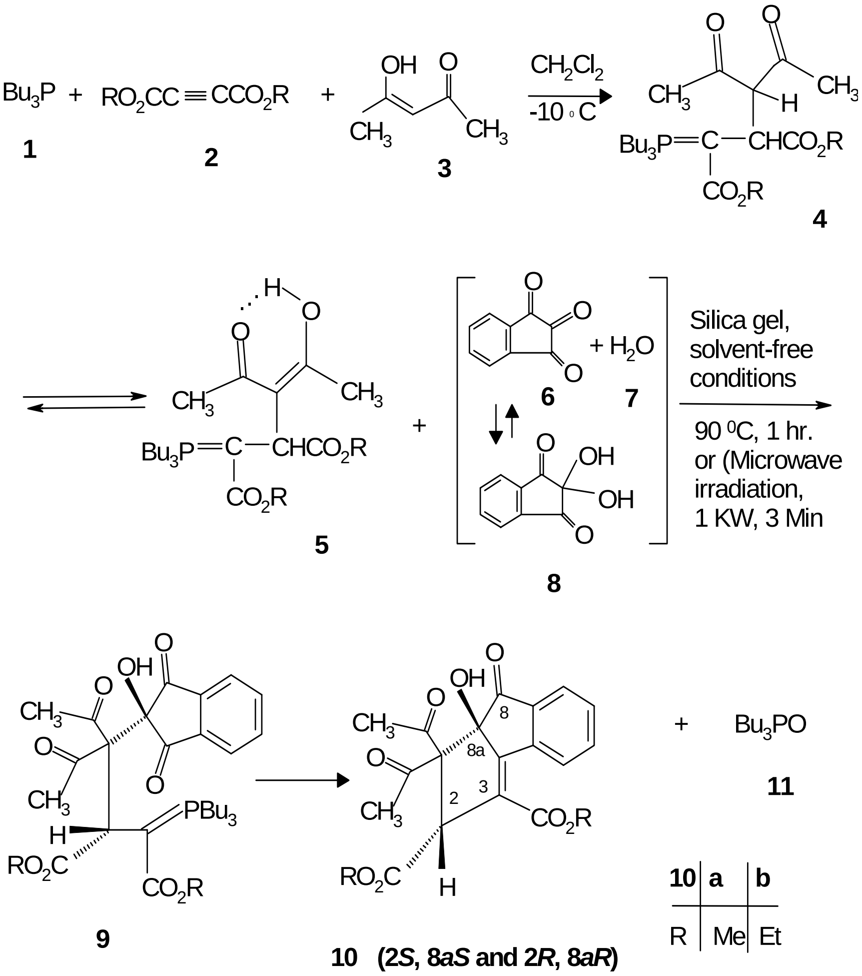
General procedure for the preparation of dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-dicarboxylates (10a-b): To a magnetically stirred solution of tributylphosphine (**1**) (1 mmol) and acetylacetone **3** (1 mmol) in CH_2Cl_2 (4 mL) was added dropwise a mixture 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**), silica gel powder (2 g) and powdered indane-1,2,3-trione [**6**, prepared from powdered ninhydrin (**8**) under thermal conditions *i.e.*, 4 h at 120ºC in oven] were heated in oven at 90ºC for 1 h (or irradiated at microwave power 1 KW for 3 min) and then 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 (**10a-b**). The characterization data of dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-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[5] on the vinylphosphonium cation to form phosphorane (**4**). Attack of the stabilized ylide **5** on the highly electron deficient carbonyl group of indane-1,2,3-trion (**6**) would lead to the stabilized ylide **9**. Intramolecular Wittig reaction of stabilized ylide **9** leads to dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-dicarboxylates (**10**) and tributylphosphine oxide (**11**) (**Scheme-1**). TLC indicated that the reactions were completed in the presence of silica gel powder in solvent-free system under thermal (after 1 h at 90ºC) and microwave conditions (after 3 min at microwave power 1KW) (**Scheme-1**). We have also used less reactive aldehydes (*p*-nitrobezaldehyde) and ketones (acetophenone) instate of indane-1,2,3-trion in this reaction, but no products were observed in the reaction conditions. TLC indicated that the solution contained ylide **4** and the starting aldehyde or ketone. The structures **10a-b** were deduced from their IR, ^{1}H and ^{13}C NMR spectra. All of these data are the as same as our previous report data[3] for the compounds **10a-b**. Since compound **10** possess two stereogenic centers, four stereoisomers (2R, 8aR; 2S, 8aS; 2R, 8aS and 2S, 8aR) are possible[3]. We have established the stereochemistry of compound **10a** (2R, 8aR and its mirror image 2S, 8aS) *via* single crystal X-ray diffraction method[6].

Conclusion

A convenient, stereoselective method for preparing dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocy-clopenta[*a*]indene-2,3-dicarboxylates (**10**) utilizing *in situ* generation of the phosphorane (**4**) in the presence of silica gel powder in solvent-free system under thermal and microwave conditions (**Scheme-1**). Other aspects of this process are under investigation.



10	a	b
R	Me	Et

Scheme-1

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