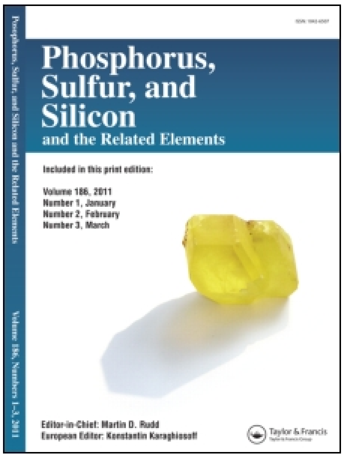

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One-Step Stereoselective Synthesis of Dialkyl 1,1-Diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-dicarboxylates from the Reaction of Dialkyl 2-(1-Acetyl-2-oxopropyl)-3-(tributylphosphoranylidene) Succinates with Indene-1,2,3-trione

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One-Step Stereoselective Synthesis of Dialkyl 1,1-Diacetyl-8*a*-hydroxy-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 Indene-1,2,3-trione

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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 that undergo an intermolecular addition reaction with indene-1,2,3-trione and concomitant intramolecular Wittig reaction in CH_2Cl_2 *at room temperature to produce dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-dicarboxylates in fairly good yields.*

Keywords Acetylacetone; acetylenic esters; indene-1,2,3-trione; intramolecular Wittig reaction; tributylphosphine

INTRODUCTION

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 preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[1] In this article, we wish to report 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** in

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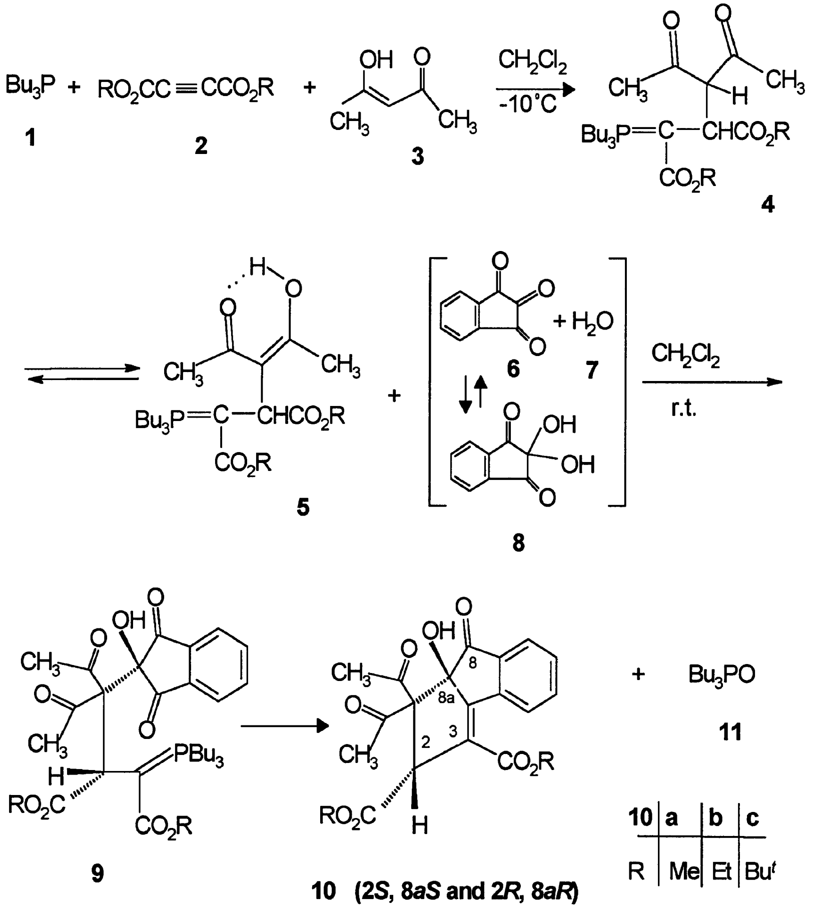

10	a	b	c
R	Me	Et	Bu^t

SCHEME 1

fairly good yields by the reaction of dialkyl 2-(1-acetyl-2-oxopropyl)-3-(tributylphosphoranylidene) succinates **4** and indene-1,2,3-trione **6** (Scheme 1).

RESULTS AND DISCUSSION

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.[3] 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 to form phosphorane **4**.[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**. An 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 CH_2Cl_2 at room temperature after 24h. We also have used less reactive aldehydes (*p*-nitrobezaldehyde and ect.) and ketones (acetophenone and ect.) instead of indane-1,2,3-trion in this reaction, but no products were observed even at reflux temperature (toluene as a solvent) after 24 h. TLC indicated that the solution contained ylide **4** and the starting aldehyde or ketone. Structures **10a–c** were deduced from their elemental analysis and their UV, IR, and ^1H and ^{13}C NMR spectra. All of these data are the same as our previous data for the compounds **10a–c**.[5] Since compound **10** possess two stereogenic centers, four stereoisomers (2R and 8aR; 2S, 8aS; 2R, 8aS, and 2S, 8aR) are possible.[5] We have proved the stereochemistry of compound **10a** (2R and 8aR and its mirror image 2S and 8aS) via single crystal X-ray diffractions method (Figures 1 and 2).[6]

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

EXPERIMENTAL

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

General Procedure for the Preparation of Dialkyl 1,1-Diacetyl-8a-Hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-dicarboxylates (10a–c)

To a magnetically stirred solution of tributylphosphine (**1**) (1 mmol) and acetylacetone **3** (1 mmol) in CH_2Cl_2 (4 mL) was added dropwise to 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 and the solvent was removed under reduced pressure. The homogeneous

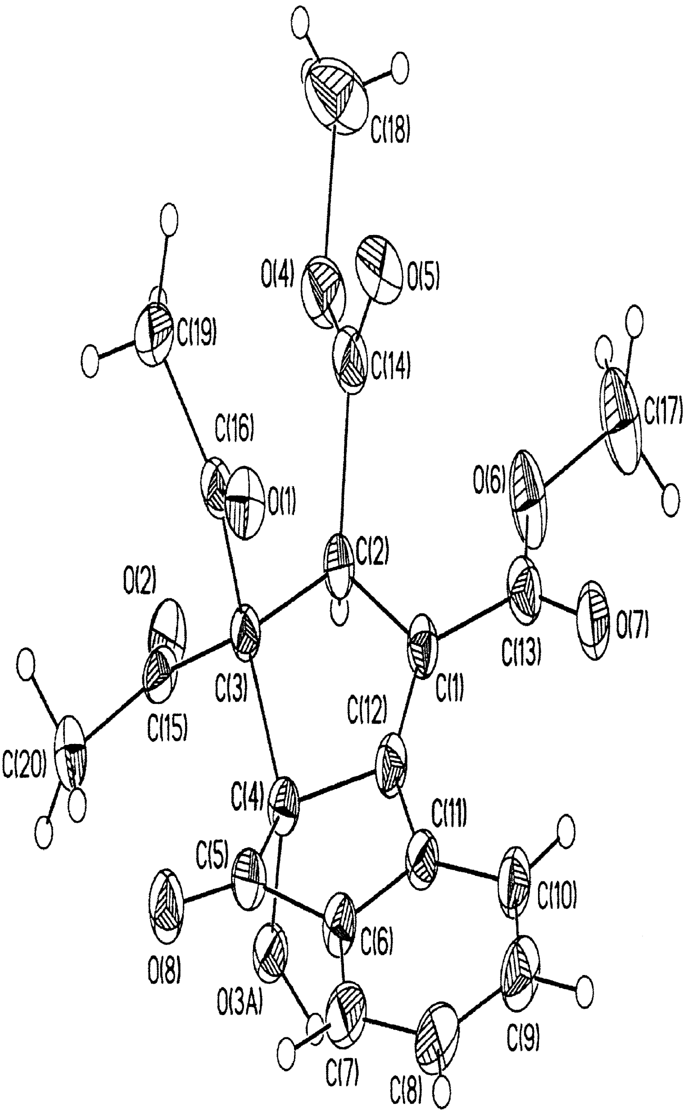

FIGURE 1 Molecular structure of **10a**.

mixture of the dried residue (ylide **4**) and powdered indane-1,2,3-trione (**6**, prepared from powdered ninhydrin **8** under thermal conditions [4 h at 120°C] in an oven) were dissolved in dry CH_2Cl_2 and stirred for 24 h. at room temperature. The solvent was removed under reduced pressure and the viscous residue was purified by flash column

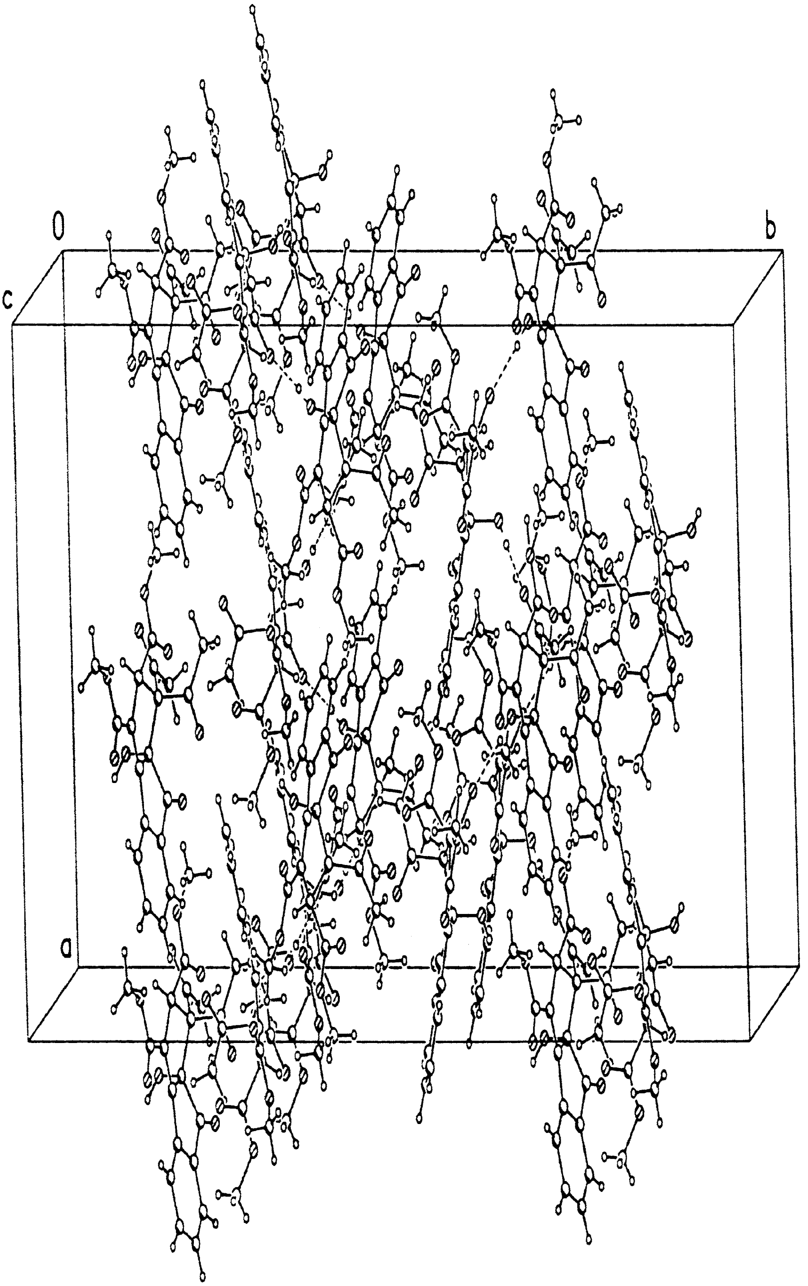

FIGURE 2 Unit cell crystal structure of **10a**.

chromatography (silica gel and ethyl acetate-light petroleum ether). The solvent was removed under reduced pressure and the products were obtained as white crystals (**10a**: mp; 180–183°C; Yield; 65%. **10b**: mp; 104–108°C; Yield; 63.5%. **10c**: mp; 163–165°C; Yield; 70%.). The characterization data of dialkyl 1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-dicarboxylates (**10a–c**) are given in our previous report.[5]

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