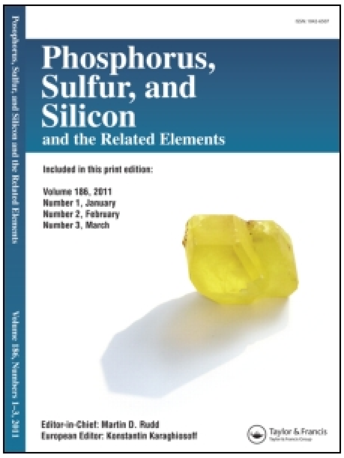

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Magnesium Sulfate Catalyzed Intermolecular Wittig Reaction of Dialkyl 2-(1-acetyl-2-oxopropyl)-3-(triphenylphosphoranylidene) Succinates with Ninhydrin in Solvent-Free Conditions

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MAGNESIUM SULFATE CATALYZED INTERMOLECULAR WITTIG REACTION OF DIALKYL 2-(1-ACETYL-2-OXOPROPYL)-3-(TRIPHENYLPHOSPHORANYLIDENE) SUCCINATES WITH NINHYDRIN IN SOLVENT-FREE CONDITIONS

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*A facial one-pot stereoselective synthesis of dialkyl 3,3-diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta[*a*]indene-1,2-dicarboxylates in fairly high yields by the intermolecular Wittig reaction of dialkyl 2-(1-acetyl-2-oxopropyl)-3-(triphenylphosphoranylidene) succinates and ninhydrin in the presence of $MgSO_4$ in solvent-free conditions at 100°C is reported.*

Keywords: Intermolecular Wittig reaction; magnesium sulfate; ninhydrin; solvent-free conditions; stabilized phosphorus ylides

A well-known method for achieving alkenylation is the Wittig reaction.[1] The area of the application of the Wittig reaction is exceedingly broad because of the possibility of changing the structure of ylide and carbonyl compound.[1] The high selectivity of the Wittig reaction enables the use of carbonyl compounds of different structures bearing different functional groups.[1] The conditions used for the Wittig reaction depend on the structures of the ylide and the carbonyl compound; the nature of the solvent, the presence of dissolved additives, the temperature, and pressure also affect the rate and stereochemistry of the Wittig reaction.[2,9] In recent years, we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[2–8] In the absence of suitable catalysts, the intermolecular Wittig reactions of the stabilized phosphorus ylides are very slow.[2,10] In this article, we report on the catalytic activity of magnesium

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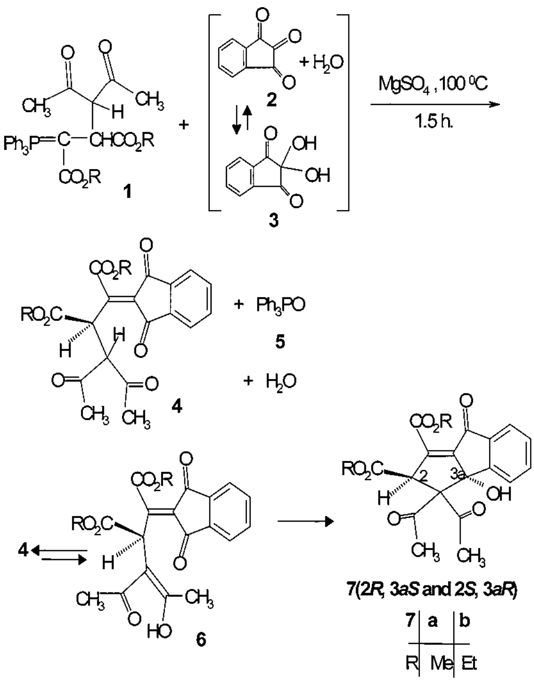

SCHEME 1

sulfate powder in the intermolecular Wittig reaction of dialkyl 2-(1-acetyl-2-oxopropyl)-3-(triphenylphosphoranylidene) succinates **1** and ninhydrin[10] **3** in the presence of $MgSO_4$ in solvent-free conditions[11,12] at 100°C in fairly high yields (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.[1] Thus, compounds **7** may be regarded as the product of an intermolecular Wittig reaction. Such olefination products may result from attack of the stabilized ylide **1** on the high electron deficient carbonyl group of indane-1,2,3-trion **2** in a normal intermolecular Wittig reaction. This would lead to the intermediate **4** and triphenylphosphine oxide **5**.[2,6,7] Annulation of the enol form of **4** (**6**) leads to dialkyl 3,3-diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta[*a*]indene-1,2-dicarboxylates **7** (Scheme 1). TLC indicated that the reactions were completed in solid phase ($MgSO_4$

powder) at 100°C after 1.5 h. We also have used $NaHSO_4$, SiO_2, Al_2O_3, MgO, ZnO, $ZnSO_4$, and $KAl(SO_4)_2$ in this reaction, but yields of the corresponding products **7** in cases of Al_2O_3, MgO, and ZnO were low and in the others cases no product were obtained and in all cases decomposition were observed. In the absence of the $MgSO_4$ powder, the mixture of powdered ylide **1** and powdered ninhydrin did not react at 100°C after 1.5 h, and decomposition of the starting materials was observed. These reactions were completed in CH_2Cl_2 after 170 h.[10] In the absence of the $MgSO_4$ powder the reactions were not completed at reflux temperature (toluene as solvent) after 24 h and decomposition of the starting materials and products were observed. We also have used less reactive aldehydes (*p*-nitrobezaldehyde, etc.) and ketones (acetophenone, etc.) instead of ninhydrin in this reaction in the presence of the $MgSO_4$ powder in the solvent-free system, but no products were observed even at 110°C or above.[2]

The structures **7a–b** were deduced from their melting points, IR, and ^{1}H NMR spectra. All of these data are the same as in our previous report for the compounds **7a–b**.[10] Since compound **7** possess two stereogenic centers, four stereoisomers (2R, 3aS; 2S, 3aR; 2R, 3aR; and 2S, 3aS) are possible.[10] We have proved the stereochemistry of compound **7a** (2R, 3aS and its mirror image 2S, 3aR) via single crystal x-ray diffraction method.[13]

In summary, we have developed a convenient, one-pot stereoselective method for preparing dialkyl 3,3-diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta[*a*]indene-1,2-dicarboxylates **7** from phosphorane **1** and ninhydrin **3** in the presence of magnesium sulfate in solvent-free system. 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. ^{1}H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz.

General Procedure for the Preparation of Dialkyl 3,3-diacetyl-3a-hydroxy-8-oxo-2,3,3a,8-tetrahydrocyclopenta[a]indene-1,2-dicarboxylates (7a–b)

The homogenous mixture of powdered ninhydrin **3** (1 mmol), powdered ylide **1** (1 mmol), and powdered anhydrous magnesium sulfate (1 g) were heated in an oven at 100°C for 1.5 h 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 the products were obtained as white crystals (**7a:** m.p. 180–183°C, yield: 89%; **7b:** m.p. 104–108°C, yield: 91%). The full characterization data of the compounds (**7a–b**) are given in our previous report.[10]

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