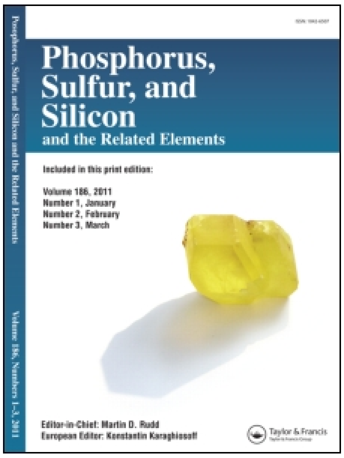

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Microwave Induced Reaction of Dialkyl 2-(1-Acetyl-2-Oxopropyl)-3-(triphenylphosphoranylidene) Succinates with Ninhydrin in the Presence of Magnesium Sulfate in Solvent-Free Conditions

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To cite this Article Ramazani, Ali(2003) 'Microwave Induced Reaction of Dialkyl 2-(1-Acetyl-2-Oxopropyl)-3-(triphenylphosphoranylidene) Succinates with Ninhydrin in the Presence of Magnesium Sulfate in Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 8, 1839 — 1844

To link to this Article: DOI: 10.1080/10426500307839

URL: http://dx.doi.org/10.1080/10426500307839

Phosphorus, Sulfur, and Silicon, 178:1839–1844, 2003

ISSN: 1042-6507 print
DOI: 10.1080/10426500390221519

MICROWAVE INDUCED REACTION OF DIALKYL 2-(1-ACETYL-2-OXOPROPYL)-3-(TRIPHENYLPHOSPHORANYLIDENE) SUCCINATES WITH NINHYDRIN IN THE PRESENCE OF MAGNESIUM SULFATE IN SOLVENT-FREE CONDITIONS

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(Received March 25, 2003)

*Microwave catalyzed one-pot stereoselective synthesis of dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-carboxylates in fairly high yields by the reaction of dialkyl 2-(1-acetyl-2-oxopropyl)-3-(triphenylphosphoranylidene) succinates and ninhydrin in the presence of $MgSO_4$ in solvent-free conditions.*

Keywords: Magnesium sulfate; microwave; ninhydrin; solvent-free conditions; Wittig reaction

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

This work was supported by the Zanjan University Research Council via research project entitled: *Synthesis of stabilized phosphoranes from CH-acids and investigation of their reactions with indene-1,2,3-trione in the presence of magnesium sulfate* (ZUARC8242).

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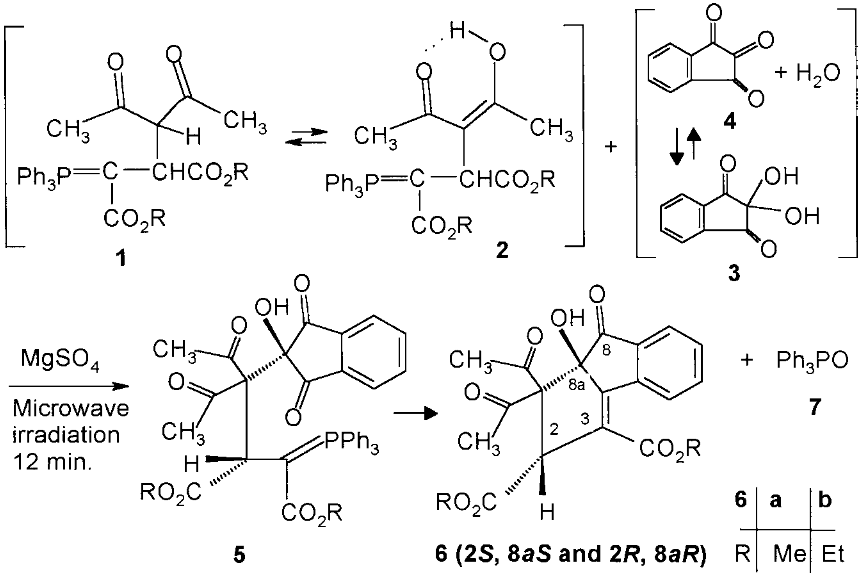

SCHEME 1

of suitable catalysts, Wittig reaction of the stabilized phosphorus ylides are very slow.[2,10] The use of microwave irradiation to bring about organic transformations has taken new dimensions in recent years.[14] In this article, we report on the catalytic action of microwave in one-pot stereoselective synthesis of dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-carboxylates in fairly high yields by the 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 (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 **6** may be regarded as the product of an intramolecular Wittig reaction. Such olefination products may result from attack of the stabilized ylide **2** on the highly electron deficient carbonyl group of indane-1,2,3-trion **4**, which would lead to the stabilized ylide **5**. Intramolecular Wittig reaction of stabilized ylide **5** leads to dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-carboxylates **6** and triphenylphosphine oxide **7** (Scheme 1).[2,6,7] TLC indicated that the reactions were completed in solid phase ($MgSO_4$ powder) under microwave irradiation at microwave power 1 KW after 12 min. In the absence of the microwave irradiation the reactions were completed at 100°C after 1.5 h.[10] 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 corresponding products **6** in cases of Al_2O_3, MgO, and ZnO were low and in the others cases no product was observed, and in all cases decomposition was observed. In the absence of the $MgSO_4$ powder, the mixture of powdered ylide **1** and powdered ninhydrin did not react under microwave irradiation at microwave power 1 KW after 12 min 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 was observed. We also have used less reactive aldehydes (*p*-nitrobezaldehyde and etc.) and ketones (acetophenone and etc.) instead of ninhydrin in this reaction in the presence of the $MgSO_4$ powder under microwave irradiation at microwave power 1 KW after 12 min or more in the solvent-free system, but no products were observed.[2]

The structures **6a-b** were deduced from their melting points, IR, and ^1H NMR spectra. All of these data are the same as our previously reported data for the compounds **6a-b**.[10] Since compound **6** possess two stereogenic centers, four stereoisomers (2R, 8aR; 2S, 8aS; 2R, 8aS and 2S, 8aR) are possible.[10] We have proved the stereochemistry of compound **6a (**2R, 8aR and its mirror image 2S, 8aS) via single crystal x-ray diffraction (Figure 1) method.[13]

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-carboxylates **6** from phosphorane **1** and ninhydrin **3** in the presence of magnesium sulfate under microwave irradiation in a solvent-free system. Other aspects of this process are under investigation.

EXPERIMENTAL

Commerical oven Butane M245 was used for microwave irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. UV spectra were recorded on a Shimadzu UV-2100 spectrophothometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra were

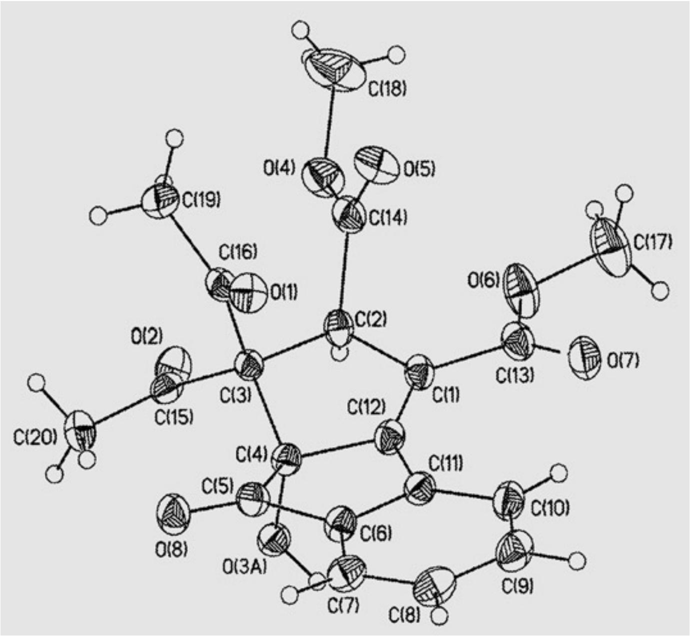

FIGURE 1 ORTEP diagram of **6a**.

measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

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-carboxylates (6a-b)

The homogeneous mixture of powdered ninhydrin **3** (1 mmol), powdered ylide **1** (1 mmol) and powdered anhydrous magnesium sulfate (1 g) were irradiated in the microwave oven at microwave power 1 KW (100%) for 12 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 (**6a-b**). The characterisation data of dialkyl 1,1-diacetyl-8*a*-hydroxy-8-oxo-1,2,8,8*a*-tetrahydrocyclopenta[*a*]indene-2,3-carboxylates (**6a-b**) are given below:

Dimethyl 1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-carboxylate (**6a**)*:* White crystals; m.p.: 180–183°C. Yield: 87%. UV (EtOH 95%) ($\lambda_{\max/\mathrm{nm}}$, $\log \varepsilon$): 220, 4.24; 227, 4.26; 277, 4.13; 284, 4.15. IR (KBr) ($\nu_{\max}$, Cm^{-1}): 3365, 3006, 2900, 1742, 1600, 1480. ^{1}H NMR ($CDCl_3$) δ_H: 1.97 and 2.62 (6 H, 2 s, 2 $COCH_3$), 3.65 (1 H, br. s, OH), 3.67 and 3.69 (6 H, 2 s, 2 OCH_3), 5.30 (1 H, s, H2); 7.62 (1 H, t, $^3J_{HH} = 7.6$ Hz); 7.76 (1 H, t, $^3J_{HH} = 7.6$ Hz); 7.87 (1 H, d, $^3J_{HH} = 7.6$ Hz); 8.46 (1 H, d, $^3J_{HH} = 7.6$ Hz). ^{13}C NMR ($CDCl_3$)δ_C: 28.66 and 29.31 (2 CH_3, ketone); 52.15 and 52.64 (2 OCH_3); 59.29 (C2); 81.46 (C1); 88.49 (C8a); 122.95, 138.76, 140.32 and 153.58 (4 C); 125.37, 129.07, 132.25, and 135.83 (4 CH); 164.00 and 170.61 (2 C=O of esters); 195.56 (C=O, ketone); 201.45 and 201.91 (2 C=O of methylketones). MS(m/z, %): 386 (M^+, 14), 344 (63); 311(50); 277(100); 225(49); 213(43); 183(27); 152(20); 115 (15); 77(8); 43(23). Found: C, 62.93; H, 5.08. $C_{20}H_{18}O_8$ requires C, 62.18; H, 5.00%.

Diethyl 1,1-diacetyl-8a-hydroxy-8-oxo-1,2,8,8a-tetrahydrocyclopenta[a]indene-2,3-carboxylate (**6b**)*:* White crystals; m.p.: 104–108°C. Yield: 85%. UV (EtOH 95%) ($\lambda_{\max/\mathrm{nm}}$, $\log \varepsilon$): 216, 4.47; 229, 4.53; 270, 4.24; 284, 4.30. IR (KBr) ($\nu_{\max}$, Cm^{-1}): 3369, 3005, 2908, 1745, 1603, 1482. ^{1}H NMR ($CDCl_3$)δ_H: 1.23 and 1.28 (6 H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et); 1.98 and 2.62 (6 H, 2 s, 2 $COCH_3$), 3.76 (1 H, br. s, OH), 4.15 and 4.23 (4 H, 2 q, $^3J_{HH} = 7.1$ Hz, 2 OCH_2 of 2 Et); 5.29 (1 H, s, H2); 7.61 (1 H, t, $^3J_{HH} = 7.7$ Hz); 7.75 (1 H, t, $^3J_{HH} = 7.7$ Hz); 7.87 (1 H, d, $^3J_{HH} = 7.7$ Hz); 8.51 (1 H, d, $^3J_{HH} = 7.7$ Hz). ^{13}C NMR ($CDCl_3$) δ_C: 13.64 and 14.05 (2 CH_3 of 2 Et); 28.89 and 29.36 (2 CH_3, ketone); 59.41 (C2); 61.46 and 61.76 (2 OCH_2); 81.41 (C1); 88.51 (C8a); 123.50, 138.88, 140.23, and 153.27 (4 C); 125.37, 129.21, 132.17, and 135.83 (4 CH); 163.67 and 170.18 (2 C=O of esters); 195.69 (C=O, ketone); 201.42 and 202.00 (2 C=O of methylketones). MS(m/z, %): 414 (M^+, 8), 371 (35); 325(64); 297(71); 278(100); 251(50); 225(30); 209(23); 149(15). Found: C, 64.01; H, 5.27. $C_{22}H_{22}O_8$ requires C, 63.76; H, 5.35%.

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