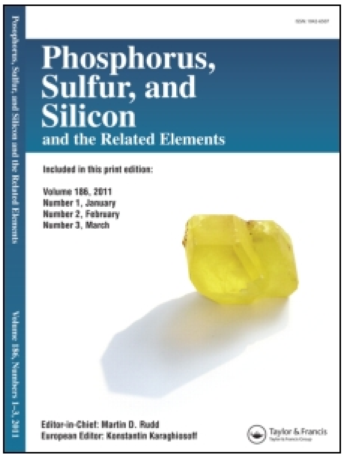

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Vinylphosphonium Salt Mediated One-Pot Stereoselective Synthesis of Dialkyl 3,3-Diacetyl-3 a -hydroxy-8-oxo-2,3,3 a ,8-tetrahydrocyclopenta-[a]indene-1,2-dicarboxylates

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VINYLPHOSPHONIUM SALT MEDIATED 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

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Protonation of the highly reactive 1:1 intermediates produced in the reaction between triphenylphosphine (or tributylphosphine) and dialkyl acetylenedicarboxylates by acetylacetone leads to sterically congested phosphorus ylides, which undergo an intermolecular Wittig reaction with ninhydrin and concomitant annulation in CH_2Cl_2 *at room temperature to produce dialkyl 3,3-diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta[*a*]indene-1,2-dicarboxylates in fairly high yields.*

Keywords: Acetylacetone; acetylenic esters; ninhydrin; tributylphosphine; triphenylphosphine; Wittig reaction

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.[1–9] In recent years, we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilising in situ generation of the phosphonium salts.[2–8] In this article, we report 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 **10** in fairly high yields (Scheme 1).

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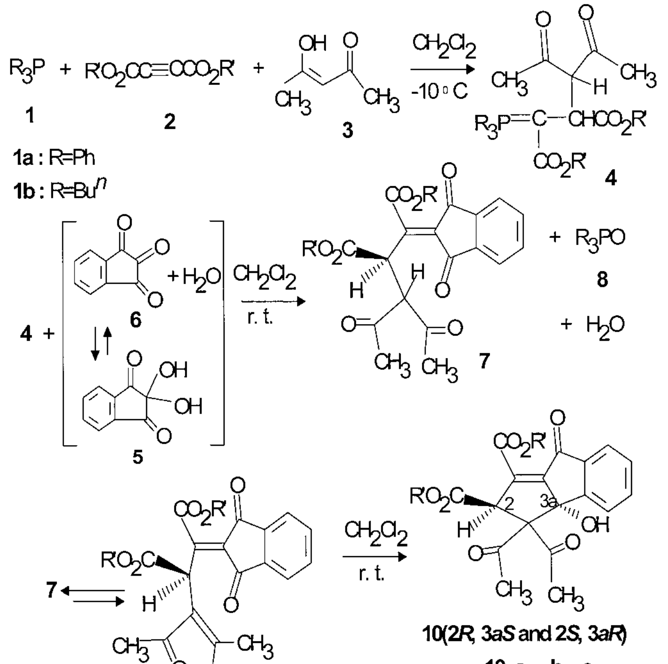

10	a	b	c
R'	Me	Et	Bu^t

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 **10** may be regarded as the product of an intermolecular Wittig reaction. Such addition-olefination products may result from an initial addition of phosphine **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**.[8] Attack of the stabilized ylide **4** on the highly electron deficient carbonyl group of indane-1,2,3-trion **6** in a normal intermolecular Wittig reaction would lead to the intermediate **7** and phosphine oxide **8**.[2,6,7] Annulation of the enol form of **7**(**9**) leads to dialkyl 3,3-diacetyl-3a-hydroxy-8-oxo-2,3,3a,8-tetrahydrocyclopenta[a]indene-1,2,-dicarboxylates **10** (Scheme 1). TLC indicated that the reactions (when R = Ph_3P) were completed in CH_2Cl_2 at room temperature after 170 h. When tributylphosphine is used instead of triphenylphosphine, the reactions were completed after 1.5 h.

It seems that the reason of the increase of the reaction rate in the tributylphosphine case relative to triphenylphosphine, is the result of less steric effects of the tributylphosphine group in comparison with the triphenylphosphine group at ylides **4** toward intermolecular Wittig reaction with indane-1,2,3-trion **6**.[9] We also have used less reactive aldehydes (acetaldehyde, *p*-nitrobezaldehyde, etc.) and ketones (acetone, acetophenone, etc.), but no products were observed even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained ylide **4** and the starting aldehyde or ketone.

The structures **10a–c** were deduced from their elemental analyses and their UV, IR, ^{1}H, and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at *m/z* of 386, 414, and 470 respectively. Since compound **10** possess two stereogenic centers, four stereoisomers (2R, 3aS; 2S, 3aR; 2R, 3aR and 2S, 3aS) are possible. Although, we have not proved the stereochemistry of compounds **10**, the geometries shown in Scheme 1 (2R, 3aS and its mirror image 2S, 3aR) are the most reasonable ones because of less steric hindrance for their formation from **9**. Preparation of single crystals of **10a** for single crystal x-ray diffraction are under progress and the results will be reported in the future.

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 **10** utilising in situ generation of the phosphorane **4**. Other aspects of this process are under investigation.

EXPERIMENTAL

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. ^{1}H and ^{13}C NMR spectra were 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 3,3-Diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta[*a*]indene-1,2-dicarboxylates (10a–c)

To a magnetically stirred solution of **1a** (or **1b**) (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 −10°C over 15 min. The mixture was allowed to warm to room temperature and powdered ninhydrin **5** (1 mmol) was added and stirred for 170 h. (R = Ph_3P) or 1.5 h. (R = Bu^t). The solvent was removed under reduced pressure and the viscous residue was purified by flash column chromatography (silica gel; ethyl acetate-light petroleum ether). The solvent was removed under reduced pressure and products were obtained as white crystals (**10a–c**). The characterisation data of dialkyl 3,3-diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta[*a*]indene-1,2-dicarboxylates (**10a–c**) follow.

*Dimethyl-3,3-diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta[*a*]indene-1,2-dicarboxylates* (**10a**): White crystals; m.p.: 180–183°C. Yield: 91%. UV (EtOH 95%) $\lambda_{max/nm}$, log ε): 220, 4.24; 227, 4.26; 277, 4.13; 284, 4.15. IR (KBr) (ν_{max}, Cm^{-1}): 3365, 3006, 2900, 1742, 1600, 1480. ^1H NMR ($CDCl_3$) δ_H: 1.97 and 2.62 (6H, 2 s, 2 $COCH_3$), 3.65 (1H, br. s, OH), 3.67 and 3.69 (6H, 2 s, 2 OCH_3), 5.30 (1H, s, H2); 7.62 (1H, t $^3J_{HH} = 7.6$ Hz); 7.76 (1H, t, $^3J_{HH} = 7.6$ Hz); 7.87 (1H, d, $^3J_{HH} = 7.6$ Hz); 8.46 (1H, 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 (C3); 88.49 (C3a); 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-3,3-diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta-[*a*]indene-1,2-dicarboxylates* (**10b**): White crystals; m.p.: 104–108°C. Yield: 93%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 216, 4.47; 229, 4.53; 270, 4.24; 284, 4.30. IR (KBr) (ν_{max}, Cm^{-1}): 3369, 3005, 2908, 1745, 1603, 1482. ^1H NMR ($CDCl_3$) δ_H: 1.23 and 1.28 (6H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et); 1.98 and 2.62 (6H, 2 s, 2 $COCH_3$), 3.76 (1H, br. s, OH), 4.15 and 4.23 (4H, 2 q, $^3J_{HH} = 7.1$ Hz, 2 OCH_2 of 2 Et); 5.29 (1H, s, H2); 7.61 (1H, t, $^3J_{HH} = 7.7$ Hz); 7.75 (1H, t, $^3J_{HH} = 7.7$ Hz); 7.87 (1H, d, $^3J_{HH} = 7.7$ Hz); 8.51 (1H, 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 (C3); 88.51 (C3a); 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%.

*Di-tert-butyl-3,3-diacetyl-3*a*-hydroxy-8-oxo-2,3,3*a*,8-tetrahydrocyclopenta[*a*]indene-1,2-dicarboxylates* (**10c**): White crystals; m.p.: 163–165°C. Yield: 88%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 240, 4.42; 270, 4.27;

279, 4.28. IR (KBr), ($\nu_{\max}$, Cm^{-1}); 3368, 3003, 2905, 1742, 1605, 1481. ^{1}H NMR ($CDCl_3$) δ_H: 1.49 and 1.68 (18H, 2 s, 2 $C(CH_3)_3$); 2.21 and 2.62 (6H, 2 s, 2 $COCH_3$), 281 (1H, br. s, OH), 5.24 (1H, s, H2); 7.60 (1H, t, $^3J_{HH} = 7.7$ Hz); 7.76 (1H, t, $^3J_{HH} = 7.7$ Hz); 7.89 (1H, d, $^3J_{HH} = 7.7$ Hz); 8.43 (1H, d, $^3J_{HH} = 7.7$ Hz). ^{13}C NMR ($CDCl_3$) δ_C: 27.94 and 28.22 (2 $OC(^{13}CH_3)_3$); 28.94 and 29.70 (2 CH_3, ketone); 60.45 (C2); 80.17 (C3); 82.52 and 82.96 (2 $O^{13}C(CH_3)_3$); 88.91 (C3a); 126.42,139.33, 139.77 and 149.55 (4 C); 125.46, 128.82, 130.88 and 135.66 (4 CH); 163.37 and 169.44 (2 C=O of esters); 195.70 (C=O, ketone): 201.76 and 201.96 (2 C=O of methylketones). MS (m/z, %): 470 (M^+, 7), 415(30): 359(57); 315(48); 298(94); 270(100); 253(48); 226(43); 148(29); 57(29). Found: C, 66.81; H, 6.29. $C_{26}H_{30}O_8$ requires C, 66.37; H, 6.43%.

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