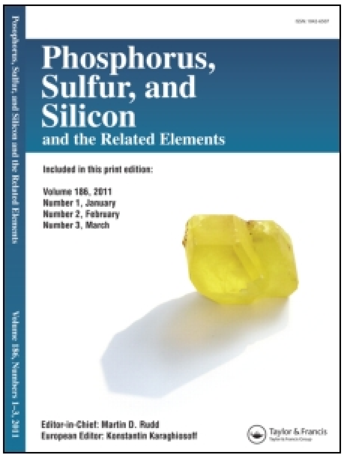

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SYNTHESIS OF HIGHLY ELECTRON-POOR ALKENES FROM IN SITU GENERATED STABILIZED PHOSPHORUS YLIDES AND NINHYDRIN *VIA* INTERMOLECULAR WITTIG REACTION

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by alcohols leads to vinyltriphenylphosphonium salts, which undergo Michael addition reaction with conjugate base to produce the corresponding stabilized phosphorus ylides. Intermolecular Wittig reaction of the stabilized phosphorus ylides with ninhydrin leads to the corresponding, highly electron-poor alkenes.

Keywords: Acetylenic ester; alcohol; intermolecular Wittig reaction; ninhydrin; triphenylphosphine

INTRODUCTION

Organophosphorus compounds have been extensively used in organic synthesis.[1–16] β-additions of nucleophiles to the vinyl group of vinylic phosphonium salts, which leads to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis.[1–16] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[1–16] In this article, we report on the one-pot synthesis of dialkyl [indane-1,3-dione-2-ylidene]alkoxysuccinates (**9**) from the reaction of alcohols (**3**), dialkyl acetylenedicarboxylates (**2**), triphenylphosphine (**1**), and ninhydrin (**6**) in low-to-good yields[5] (Scheme 1).

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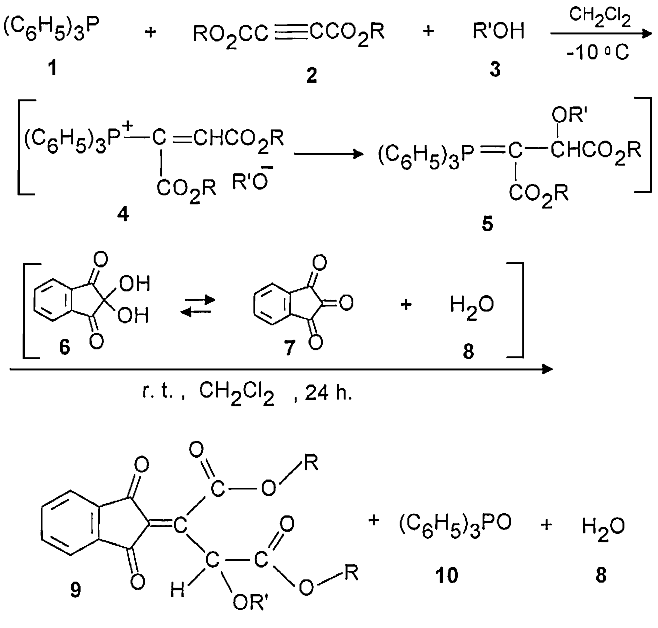
RESULTS AND DISCUSSION

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.[17–23] Thus, compounds **8** may be regarded as the product of an intermolecular Wittig reaction. Such addition-olefination products may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by attack of the alkoxide on the vinylphosphonium cation to form phosphorane **5**. Attack of the stabilized ylide **5** on the highly electron-deficient carbonyl group of indane-1,2,3-trione **7** in a normal intermolecular Wittig reaction would lead to the dialkyl [indane-1,3-dione-2-ylidene]alkoxysuccinates **9**(Scheme 1). TLC indicated that the reaction was completed after 24 h in CH_2Cl_2 at room temperature. The reaction proceeds smoothly and cleanly under mild conditions, and no



9	a	b	c	d	e	f	g	h
R	Me	Et	*t*-Bu	Me	Me	Me	Me	Me
R'	Me	Me	Me	Benzyl	Allyl	Et	*i*-Pr	*n*-Bu
%Yield	68	65	70	66	63	7	9	6

SCHEME 1

side reactions were observed. We have also used less-reactive aldehydes (benzaldehyde and 4-nitrobenzaldehyde) and ketones (acetone and acetophenone) in this reaction, but no products were observed even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained ylide **5** and the starting aldehyde or ketone. In this reaction, in the cases of EtOH, *i*-PrOH, and *n*-BuOH, the yields of the corresponding products **9** were very low (Scheme 1). The weak acidity of these alcohols may be the factor in the reduction of yields (Scheme 1).

In summary, we have developed a convenient, one-pot method for preparing dialkyl [indane-1,3-dione-2-ylidene]alkoxysuccinates **9** utilizing in situ generation of the phosphorane **5** (Scheme 1). Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Ultraviolet (UV) spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Infrared (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 [Indane- 1,3-dione-2-ylidene]alkoxysuccinates (9a–h)

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and **3** (1 mmol) in CH_2Cl_2 (5 ml) was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (5 ml) at −10°C over 15 min. The mixture was allowed to warm up to room temperature, and then powdered ninhydrin **6** (0.18 g, 1 mmol) was added and stirred for 24 h. The solvent was removed under reduced pressure, and the viscous residue was purified by flash column chromatography (silica gel; hexane-ethyl acetate). The solvent was removed under reduced pressure and the products were obtained as white crystals (**9a**, m.p. 115.5–117.5°C; **9c**, m.p. 130.9–132.9°C) and viscous colorless oils (**9b**, **9d–h**).

Spectral Data for Dimethyl [Indane-1,3-dione-2-ylidene]-methoxysuccinate (9a)

UV (ethanol, 95%), λ_{max}/nm (logε): 206 (4.02), 247 (4.26), and 281 (4.12). IR (KBr) (ν_{max}, cm^{-1}): 2960, 1749, and 1718. ^{1}H NMR (CDCl$_3$) δ_H: 0.9

and 1.3 (2H, 2 br. s, 2 OH), 3.15, 3.76 and 3.86 (9H, 3 s, 3 OCH_3), 5.97 (1H, s, OCH), 7.67 (1H, t, $^3J_{HH}$ = 7.5 Hz, CH (arom.)), 7.79 (1H, t, $^3J_{HH}$ = 7.5 Hz, CH (arom.)), 7.86 (1H, d, $^3J_{HH}$ = 7.6 Hz , CH (arom.)), 8.28 (1H, d, $^3J_{HH}$ = 7.7 Hz, CH (arom.)). ^{13}C NMR ($CDCl_3$) δ_C: 52.64, 52.80, 53.27, 90.10, 114.26, 122.88, 125.73, 128.52, 132.80, 136.36, 138.55, 140.63, 149.41, 162.43, 168.60 and 190.03. MS, *m/z(%)*: 318 (M^+, 30), 290 (32), 274 (60), 259 (54), 243 (100), 231 (90), 187 (20), 157 (38), 129 (30), 75 (17), and 59 (73). Analysis: Calc. for $C_{16}H_{14}O_7$(318.28): C, 60.38; H, 4.43. Found: C, 60.32; H, 4.68.

Spectral Data for Diethyl [Indane-1,3-dione-2-ylidene]-methoxysuccinate (9b)

UV (ethanol, 95%), λ_{max}/nm (logε): 206 (4.09), 246 (4.25), and 279 (4.13). IR (KBr) (ν_{max}, cm^{-1}): 2991, 1749, and 1720. ^{1}H NMR ($CDCl_3$) δ_H : 1.05, and 1.14 (2 H, 2 br. s, 2 OH), 1.20, and 1.29 (6H, 2 t, $^3J_{HH}$ = 7.1 Hz, 2 CH_3 of 2 Et); 3.44 (3H, s, OCH_3), 4.1–4.3 (4H, 2 m, 2 OCH_2 of 2 Et), 5.90 (1H, s, OCH), 7.57 (1H, t, $^3J_{HH}$ = 7.5 Hz, CH (arom.)), 7.72 (1H, t, $^3J_{HH}$ = 7.5 Hz, CH (arom.)), 7.78 (1H, d, $^3J_{HH}$ = 7.6 Hz , CH (arom.)), 8.23 (1H, d, $^3J_{HH}$ = 7.7 Hz, CH (arom.)). ^{13}C NMR ($CDCl_3$) δ_C: 14.30, 14.48, 52.65, 61.92, 62.31, 90.27, 114.30, 123.37, 125.71, 128.67, 132.68, 136.27, 138.57, 140.48, 149.02, 161.93, 168.20, and 190.12.

Spectral Data for di-tert-butyl [Indane-1,3-dione-2-ylidene]methoxysuccinate (9c)

UV (ethanol, 95%), λ_{max}/nm (logε): 204.8 (3.69), 247.2 (3.79) and 280.0 (3.99). IR (KBr) (ν_{max}, cm^{-1}): 2978, 2930, 1738, and 1700. ^{1}H NMR ($CDCl_3$) δ_H : 1.43, and 1.55 (18H, 2 s, 2 OC $(CH_3)_3$), 3.49 (3H, s, OCH_3), 5.77 (1H, s, OCH), 7.59 (1H, t, $^3J_{HH}$ = 7.6 Hz, CH (arom.)), 7.75 (1H, t, $^3J_{HH}$ = 7.6 Hz, CH (arom.)), 7.83 (1H, d, $^3J_{HH}$ = 7.6 Hz, CH (arom.)), 8.29 (1H, d, $^3J_{HH}$ = 7.6 Hz, CH (arom.)). ^{13}C NMR ($CDCl_3$) δ_C: 28.18, 28.50, 52.52, 82.87, 83.39, 91.95, 114.59, 125.20, 125.51, 128.71, 132.20, 136.05, 139.04, 140.32, 147.36, 161.48, 167.26, and 190.71. MS, *m/z* (%): 402 (M^+, 6), 371 (28), 347 (42), 315 (45), 291 (55), 271 (16), 258 (14), 245 (30), 228 (42), 57 (100%), 41 (32). Analysis: Calc. for $C_{22}H_{26}O_7$ (402.45): C, 65.66; H, 6.51. Found: C, 65.23; H, 6.55.

Spectral Data for Dimethyl [Indane-1,3-dione-2-ylidene]benzoxysuccinate (9d)

UV (ethanol, 95%), λ_{max}/nm (logε): 207 (4.02), 247 (3.98), and 282 (3.85). IR (KBr) (ν_{max}, cm^{-1}): 2980, 1757, and 1720. ^{1}H NMR ($CDCl_3$) δ_H: 1.1

and 1.4 (2H, 2 br. s, 2 OH), 3.75 and 3.82 (6H, 2 s, 2 OCH_3), 4.72 (1H, d, $^2J_{HH} = 9.0$ Hz, OCH_2), 4.98 (1H, d, $^2J_{HH} = 9.0$ Hz, OCH_2), 5.98 (1H, s, OCH), and 7.0–8.4 (9H, m, 9 CH (arom.)). ^{13}C NMR ($CDCl_3$) δ_C: 52.33, 52.90, 67.35, 89.67, 113.73, 122.57, 125.38, 126.97, 127.54, 128.03, 128.47, 132.42, 136.01, 136.94, 138.25, 140.24, 149.32, 162.07, 168.22, and 189.88.

Spectral Data for Dimethyl [Indane-1,3-dione-2-ylidene]alloxysuccinate (9e)

UV (ethanol, 95%), λ_{max}/nm (logε): 206 (4.16), 247 (4.31), and 282 (4.16). IR (KBr) (ν_{max}, cm^{-1}): 2929, 2860, 1757, and 1721. ^1H NMR ($CDCl_3$) δ_H: 1.1 and 1.3 (2H, 2 br. s, 2 OH), 3.78 and 3.91 (6 H, 2 s, 2 OCH_3), 4.2–4.4 (2H, m,OCH_2), 5.0–5.4 (2H, m, $=CH_2$), 5.6–5.8 (1H, m, =CH), 6.01 (1H, s, OCH) and 7.2–8.4 (4H, m, 4 CH (arom.)). ^{13}C NMR ($CDCl_3$) δ_C: 52.33, 52.86, 66.17, 89.59, 113.53, 117.68, 133.56, 152.34, 128.31, 132.38, 135.97, 122.53, 138.17, 140.24, 149.24, 162.07, 168.18, and 189.76.

Spectral Data for Dimethyl [Indane-1,3-dione-2-ylidene]ethoxysuccinate (9f)

^1H NMR ($CDCl_3$) δ_H: 1.24 (3H, t, $^3J_{HH} = 6.8$ Hz, CH_3 of Et); 3.79 and 3.95 (6H, 2 s, 2 OCH_3), 3.85 (2H, q, $^3J_{HH} = 6.8$ Hz, OCH_2 of Et); 6.01 (1H, s, OCH), and 7.5–8.4 (4H, m, 4 CH (arom.)).

Spectral Data for Dimethyl [Indane-1,3-dione-2-ylidene]iso-propoxysuccinate (9g)

^1H NMR ($CDCl_3$) δ_H: 1.11 (3H, d, $^3J_{HH} = 6.8$ Hz, CH_3 of *iso*-propyl); 1.33 (3H, d, $^3J_{HH} = 6.8$ Hz, CH_3 of *iso*-propyl), 3.80 and 3.91 (6H, 2 s, 2 OCH_3), 4.2–4.5 (1H, m, OCH of *iso*-propyl), 6.00 (1H, s, OCH), and 7.5–8.3 (4H, m, 4 CH (arom.)).

Spectral Data for Dimethyl [Indane-1,3-dione-2-ylidene]butoxysuccinate (9h)

^1H NMR ($CDCl_3$) δ_H: 0.8–1.0 (7H, m, *n*-butyl), 1.0–1.3 (2H, 2 br. s, 2 OH), 3.7–4.0 (8H, m, 2 OCH_3 and 1 OCH_2), 5.98 (1H, s, OCH) and 7.5–8.4 (4H, m, 4 CH (arom.)).

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