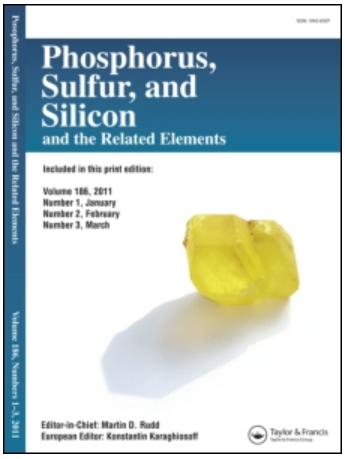

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One-Step Synthesis of Electron-Poor Alkenes from Triphenylphosphine, Acetylenic Esters, 2,2,2-Trichloroethanol, and Ninhydrin

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One-Step Synthesis of Electron-Poor Alkenes from Triphenylphosphine, Acetylenic Esters, 2,2,2-Trichloroethanol, and Ninhydrin

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 2,2,2-trichloroethanol leads to vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce the corresponding chlorine-containing stabilized phosphorus ylides. An intermolecular Wittig reaction of the chlorine-containing stabilized phosphorus ylides with ninhydrin leads to the corresponding highly electron-poor chlorine-containing alkenes.

Keywords 2,2,2-trichloroethanol; acetylenic ester; intermolecular Wittig reaction; ninhydrin; triphenylphosphine

INTRODUCTION

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] Organophosphorus compounds have been extensively used in organic synthesis.[1–3] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing the in situ generation of the phosphonium salts.[1] In this article, we report on the one-pot synthesis of dialkyl 2-(1,3-dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trichloroethoxy)succinates (**9**)

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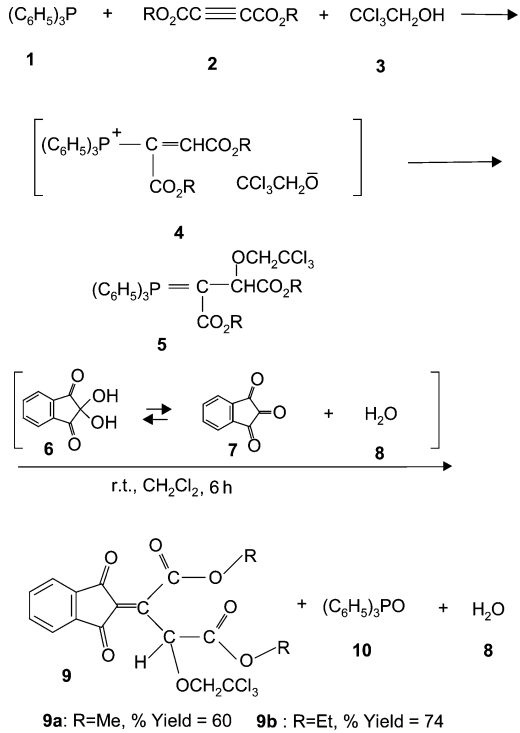
from the reaction of 2,2,2-trichloroethanol (**3**), dialkyl acetylenedicarboxylates (**2**), triphenylphosphine (**1**), and ninhydrin (**6**) in fairly high yields[3] (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

Reactions are known in which a α,β-unsaturated carbonyl compound is produced from a phosphorane and a carbonyl compound, such as an aldehyde or ketone.[4–10] Thus, compounds **9** 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 anion of 2,2,2-trichloroethanol on the vinylphosphonium cation to form phosphorane **5**. An attack of the chlorine-containing stabilized phosphorus 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 2-(1,3-dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trichloroethoxy)succinates **9** (Scheme 1). TLC

indicated that the reaction was completed after 6 h in CH_2Cl_2 at r.t. The reaction proceeded smoothly and cleanly under mild conditions, and no side reactions were observed. We have also used fairly 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 a solvent) after 24 h. TLC indicated that the solution contained ylide **5** and the starting aldehyde or ketone.

CONCLUSION

In summary, we have developed a convenient, one-pot method for the preparation of dialkyl 2-(1,3-dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(2,2,2-trichloroethoxy)succinates **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. 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.

General Procedure for the Preparation of Dialkyl 2-(1,3-Dioxo-1,3-dihydro-2H-indan-2-yliden)-3-(2,2,2-trichloroethoxy)succinates (9a–b)

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and 2,2,2-trichloroethanol **3** (0.15 g, 1 mmol) in CH_2Cl_2 (4 mL) was added dropwise a mixture of **2** (0.13 mL, 1 mmol) in CH_2Cl_2(4 mL) at -10°C over 15 min. The mixture was allowed to warm up to r.t.; powdered ninhydrin **6** (0.36 g, 2 mmol) was added and stirred for 6 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 solids (**9a**, m.p. 134–138°C; **9b**, m.p. 109–111°C).

Spectral Data for Dimethyl 2-(1,3-Dioxo-1,3-dihydro-2H-indan-2-yliden)-3-(2,2,2-trichloroethoxy)succinate (9a)

IR(KBr) (ν_{max}, cm^{-1}): 3432, 2923, 2861, 1751, 1727, 1597, 1443 and 1280. ^{1}H NMR($CDCl_3$) δ_H: 3.78 and 3.88 (6 H, 2 s, 2 OCH_3), 4.31 and

4.54 (2 H, 2d, $^2J_{HH} = -11.1$ Hz, $OCH_AH_BCCl_3$), 6.08 (1 H, s, OCH), 7.66 (1 H, t, $^3J_{HH} = 7.6$ Hz, CH(arom.)), 7.81(1H, t, $^3J_{HH} = 7.6$ Hz, CH(arom.)), 7.88(1 H, d, $^3J_{HH} = 7.6$ Hz, CH(arom.)), 8.33 (1 H, d, $^3J_{HH} = 7.6$ Hz, CH(arom.)). ^{13}C NMR($CDCl_3$)) δ_C: 52.44 and 52.98 (2 OCH_3), 76.31(OCH_2), 90.08(OCH), 95.91(CCl_3)), 112.90, 123.46, 148.35, 125.57, 128.52, 132.63, 136.44, 138.27, 139.89, 161.92, 167.76 and 189.01.

Spectral Data for Diethyl 2-(1,3-Dioxo-1,3-dihydro-2H-indan-2-yliden)-3-(2,2,2-trichloroethoxy)succinate (9b)

IR(KBr) (ν_{max}, cm^{-1}): 3455, 2985, 2939, 1743, 1596, 1450 and 1295. ^{1}H NMR($CDCl_3$)δ_H: 1.28 and 1.36 (6 H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et), 4.1–4.4 (4 H, m, 2 OCH_2 of 2 Et), 4.32 and 4.54 (2 H, 2d, $^2J_{HH} = -11.1$ Hz, $OCH_AH_BCCl_3$), 6.05 (1H, s, OCH), 7.65 (1 H, t, $^3J_{HH} = 7.7$ Hz, CH(arom.)), 7.81(1H, t, $^3J_{HH} = 7.7$ Hz, CH(arom.)), 7.87(1 H, d, $^3J_{HH} = 7.7$ Hz, CH(arom.)), 8.34 (1 H, d, $^3J_{HH} = 7.7$ Hz, CH(arom.)). ^{13}C NMR($CDCl_3$) δ_C: 13.98 and 14.16 (2 CH_3); 62.69 and 62.14 (2 OCH_2), 76.30(OCH_2), 90.35(OCH), 95.95(CCl_3)), 112.97, 124.03, 148.11, 125.51, 128.61, 132.50, 136.34, 138.39, 139.85, 161.51, 167.37 and 189.14.

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