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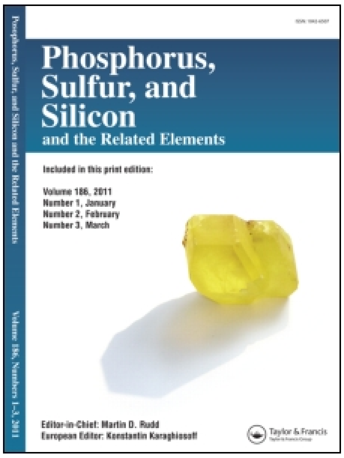

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 4-(trifluoromethyl)benzyl alcohol leads to vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce the corresponding fluorine-containing stabilized phosphorus ylides. An intermolecular Wittig reaction of the fluorine-containing stabilized phosphorus ylides with ninhydrin leads to the corresponding highly electron-poor fluorine-containing alkenes.

Keywords 4-(Trifluoromethyl)benzyl alcohol; acetylenic ester; intermolecular Wittig reaction; ninhydrin; triphenylphosphine

INTRODUCTION

Organophosphorus compounds have been extensively used in organic synthesis.[1–3] 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.[1–3] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of 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-(4-(trifluoromethyl)benzyloxy)succinates (**9**) from the reaction of 4-(trifluoromethyl)benzyl alcohol (**3**),

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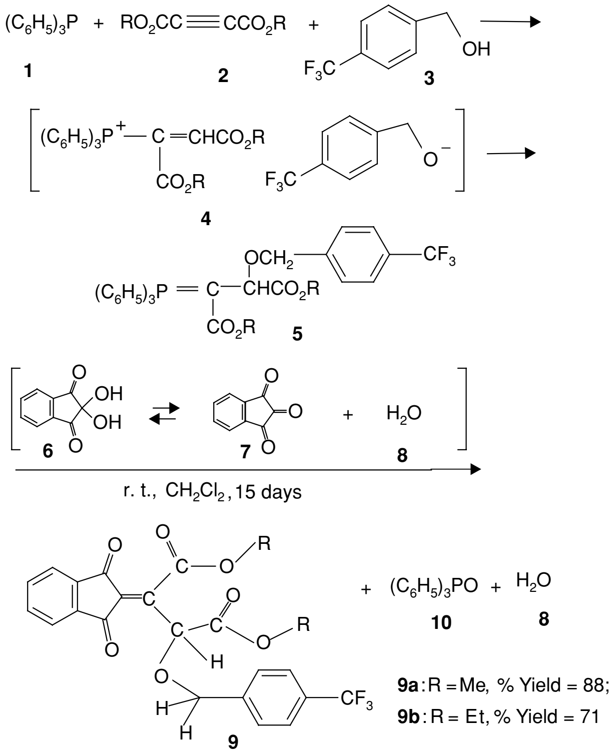
Address correspondence to Ali Ramazani, Chemistry Department, Zanjan University, PO Box 45195-313, Zanjan, Iran. E-mail: aliramazani@yahoo.com dialkyl acetylenedicarboxylates (**2**), triphenylphosphine (**1**), and ninhydrin (**6**) in fairly high yields (Scheme 1).



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, compound **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 an attack of the anion of 4-(trifluoromethyl)benzyl alcohol on the vinylphosphonium cation to form phosphorane **5**. An attack of the flourine-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 dialkyl 2-(1,3-dioxo-1,3-dihydro-2*H*-indan-2-yliden)-3-(4-(trifluoromethyl)benzyloxy)succinates **9** (Scheme 1). TLC indicated that the reaction was completed after 15 days in CH_2Cl_2 at r.t. Formation of sterically congested alkenes **9** from highly stabilized phosphorus ylides **5** may be the factors in increasing the reaction times. 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-(4-(trifluoromethyl)benzyloxy)succinates **9** utilizing in situ generation of 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. UV spectra were recorded on a Shimadzu UV-160 spectrophotometer. IR spectra were recorded on a Mattson 1000 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Spectrospin spectrometer at 250 and 62.5 MHz, respectively.

General Procedure for the Preparation of Dialkyl 2-(1,3-dioxo-1,3-dihydro-2H-indan-2-yliden)-3-(4-(trifluoromethyl)-benzyloxy)succinates (9a–b)

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and 4-(trifluoromethyl)benzyl alcohol **3** (0.14 g, 1 mmol) in CH_2Cl_2 (3 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 r.t., powdered ninhydrin **6** (0.18 g, 1 mmol) was added and stirred for 15 days. 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. 126.0–127.5°C; **9b**, m.p. 111.0–112.0°C).

Spectral Data for Dimethyl 2-(1,3-dioxo-1,3-dihydro-2H-indan-2-yliden)-3-(4-(trifluoromethyl)benzyloxy)succinate (9a)

UV (EtOH 95%) ($\lambda_{\max/\mathrm{nm}}$, log ε): 211, 3.98; 247, 4.06; 281, 3.91. IR(KBr) ($\nu_{\max}$, cm^{-1}): 3440, 2965, 1758, 1727, 1443 and 1241. ^{1}H NMR(CDCl$_3$) δ_H 3.77 and 3.86 (6H, 2s, 2OCH$_3$); 4.78 and 4.99 (2H, 2d,$^{3}J_{HH}$ = 12.0 Hz, OCH$_2$); 5.96 (1H, s, OCH); 7.35 and 7.54 (4H, 2d,$^{3}J_{HH}$ = 8.0 Hz, arom.); 7.67(1H, t,$^{3}J_{HH}$ = 7.5 Hz, CH, arom.); 7.82 (1H, t, $^{3}J_{HH}$ = 7.5 Hz, CH, arom.); 7.88 (1H, d, $^{3}J_{HH}$ = 7.5 Hz, CH, arom.); 8.26 (1H, d, $^{3}J_{HH}$ = 7.5 Hz, CH, arom.). ^{13}C NMR(CDCl$_3$) δ: 52.41 and 52.96 (2OCH$_3$); 66.39 (OCH$_2$); 89.74 (OCH); 113.57 (1C, arom.); 126.18 (CF$_3$, q, $^{1}J_{CF}$ = 270 Hz); 122.70 and 149.06 (2C, C=C); 125.33 (2 CH, q, $^{3}J_{CF}$ = 3.7 Hz, arom.); 125.45, 127.88, 128.34, 132.51 and 136.17 (5CH, arom.); 130.03 (C, q, $^{2}J_{CF}$ = 31 Hz, arom.); 138.18, 140.08 and 141.03 (3C, arom.); 161.97 and 168.01 (2C=O, ester); 189.88 (2 C=O, ketone).

Spectral Data for Diethyl 2-(1,3-dioxo-1,3-dihydro-2H-indan-2-yliden)-3-(4-(trifluoromethyl)benzyloxy)succinate (9b)

UV (EtOH 95%) ($\lambda_{\max/}$nm, log ε): 214, 4.16; 246, 4.17; 281, 4.02. IR(KBr) ($\nu_{\max}$, cm^{-1}): 3455, 2985, 2931, 1727, 1457 and 1249. ^{1}H NMR(CDCl$_3$) δ_H 1.28 and 1.35 (6H, 2t,$^{3}J_{HH}$ = 7.5 Hz, 2CH$_3$); 4.1–4.4 (4H, m, 2OCH$_2$); 4.78 and 4.99 (2H, 2d,$^{3}J_{HH}$ = 12.0 Hz, OCH$_2$); 5.941 (1H, s, OCH); 7.35 and 7.55 (4H, 2d,$^{3}J_{HH}$ = 8.0 Hz, arom.); 7.65 (1H, t, $^{3}J_{HH}$ = 7.7 Hz, CH, arom.); 7.81 (1H, t, $^{3}J_{HH}$ = 7.7 Hz, CH, arom.); 7.87 (1H, d, $^{3}J_{HH}$ = 7.7 Hz, CH, arom.); 8.28 (1H, d, $^{3}J_{HH}$ = 7.7 Hz, CH, arom). ^{13}C NMR(CDCl$_3$) δ: 14.3 and 14.28 (2CH$_3$); 61.6 and 62.19 (2OCH$_2$); 66.4 (OCH$_2$Ph); 90.1 (OCH); 114.3 (1C, arom.); 126.18 (CF$_3$, q, $^{1}J_{CF}$ = 270 Hz); 122.7 and 148.88 (2C, C=C); 125.33 (2 CH, q, $^{3}J_{CF}$ = 3.7 Hz, arom.); 125.45, 127.88, 128.34, 132.51 and 136.17 (5CH, arom.); 130.03 (C, q, $^{2}J_{CF}$ = 31 Hz, arom.); 138.18, 140.08 and 141.03 (3C, arom.); 161.71 and 167.37 (2C=O, ester); 189.8 (2C=O, ketone).

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