SYNTHESIS OF HIGHLY FUNCTIONALIZED PHOSPHORUS YLIDES 
BY ONE-POT AND THREE-COMPONENT REACTION

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ABSTRACT
Three-component reaction between dialkyl acetylenedicarboxylate and triphenylphosphine in the presence of NH-acids including 5-fluoroisatin and 5-benzylidene-2-thioxothiazolidin-4-one leads to vinylphosphonium salts which undergo Michael addition with the conjugate base of the NH-acid to produce highly functionalized, salt-free phosphorus ylides in excellent yields.

Keywords: Phosphorus Ylides, Dialkyl Acetylenedicarboxylates, Triphenylphosphine, NH-acids

INTRODUCTION
Phosphorus ylides are reactive systems, which take part in many reactions of value in organic synthesis (Engel, 1988; Corbridge, 1995; Cadogan, 1979). Organophosphorus compounds bearing a carbon atom bound directly to a phosphorus atom, are synthetic targets of interest, at least because of their value for a variety of industrial, biological and chemical synthetic uses (Engel, 1988; Corbridge, 1995; Cadogan, 1979). Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of an appropriate phosphonium salt with a base; the corresponding phosphonium salts are usually obtained from the phosphine and an alkyl halide (Engel, 1988; Corbridge, 1995). Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins (Engel 1988; Corbridge 1995). Reaction of acetylenic esters with triphenylphosphine in the presence of an organic compound possessing an acidic-hydrogen has been recently reported to produce phosphorus ylides (Yavari and Karimi, 2007; Islami et al., 2009; Alizadeh et al., 2009). In continuation of our work on the reaction between trivalent phosphorus nucleophiles and acetylenic esters in the presence of organic NH, OH, or CH-acids (Anary-Abbasinejad et al., 2007; 2008; Mosslemin et al., 2010), we report herein the results of our study on the reaction between dialkyl acetylenedicarboxylate and triphenylphosphine in the presence of NH-acids including 5-fluoroisatin and 5-benzylidene-2-thioxothiazolidin-4-one.

MATERIALS AND METHODS
Melting points were determined with an Electrothermal 9100 apparatus. Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ¹H, ¹³C, ³¹P and ¹⁹F NMR spectra were recorded on BRUKER DRX-400 AVANCE spectrometer in CDCl₃ using TMS as internal standard. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

General Procedure
To a magnetically stirred solution of 5-fluoroisatin or 5-benzylidene-2-thioxothiazolidin-4-one (1 mmol) and triphenylphosphine (1 mmol) in acetone (15 mL) was added dialkyl acetylenedicarboxylate (1 mmol) acetone in (3 mL) at room temperature over 2 min. The reaction mixture was then allowed to stir for 2 h. The solvent was evaporated at reduced pressure. The residue was precipitated in a solution of diethylether-hexane. The solid was filtered and washed with diethyl ether to give the pure product.

Dimethyl 2-(5-fluoro-2,3-dioxo-2,3-dihydroindol-1-yl)-3-triphenylphosphanylidene) succinat (3a):
Yellow powder; m.p. 137-139° C. IR (KBr) (vmax, cm⁻¹): 1722, 1672, 1643 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 3.07 (3H, s, OCH₃), 3.85 (3H, s, OCH₃), 6.06 (1H, d, ³JPH = 16 Hz), 7.35-7.87 (18H, m,
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**RESULTS AND DISCUSSION**

The reaction of the dialkyl acetylenedicarboxylate 2 and triphenylphosphine in the presence of NH-acids including 5-fluoroisatin 1 and 5-benzylidene-2-thioxothiazolidin-4-one 4 leads to the corresponding ylides 3 and 5 in good yields (Figure 1).
Figure 1: Condensation of dialkyl acetylenedicarboxylate and triphenylphosphine in the presence of NH-acids including 5-fluoroisatin and 5-benzylidene-2-thioxothiazolidin-4-one

The products 3a,b and 5a,b were all new compounds. Their structures were deduced from their elemental analyses and spectral data.

The $^1$H NMR spectrum of 3a exhibits two sharp lines at $\delta = 3.07$ and 3.85 ppm for the protons of two methoxy groups and a doubled signal for the methine proton at 6.06 ppm ($^3$J$_{HP} = 16$ Hz). Aromatic protons resonate between 7.35 and 7.87 ppm as multiplets. $^{13}$C NMR spectra of compound 3a shows 18 distinct signals, which is consistent with the proposed structure. The $^{31}$P NMR spectrum of compound 3a consists of one signal at 23.48 ppm. This shift is similar to those observed for other stable phosphorus ylides (Tebby, 1987; Vedejs and Snoble, 1973). The structural assignments made on the basis of the NMR spectra of compounds 3a,b and 5a,b are supported by their IR spectra. The carbonyl groups exhibited...
strong absorption bands at 1722, 1672 and 1643 cm\(^{-1}\). The \(^{19}\text{F}\) NMR spectrum of compound 3a consists of one signal at -119.72 ppm.

It is reasonable to assume that ylide 3 results from the initial addition of triphenylphosphine to acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acidic 5-fluoroisatin 1 or 5-benzylidene-2-thioxothiazolidin-4-one 4. The positively charged ion 6 is then attacked by anion 7 to form the phosphorane 3 (Figure 2).

![Figure 2: Suggested mechanism for formation of compound 3 or 5](image)

In summary simple, one-pot and three-component reaction between dialkyl acetylenedicarboxylate and triphenylphosphine in the presence of NH-acids including 5-fluoroisatin and 5-benzylidene-2-thioxothiazolidin-4-one derivatives leads to highly functionalized, salt-free phosphorus ylides in excellent yields. The present method carries the advantage that the reaction is performed under neutral conditions and starting materials can be mixed without any activation or modification.

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REFERENCES


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