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Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis of Alkyl 2-(2-Oxo-1,2-dihydronaphtho [2,1-b]thiophen-1-yl)-2-

(1,1,1-triphenyl-λ⁵phosphanylidene)acetates from Triphenylphosphine, Acetylenic Esters, and 2-Naphthalenethiol

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Synthesis of Alkyl 2-(2-Oxo-1,2-dihydronaphtho [2,1-b]thiophen-1-yl)-2-(1,1,1-triphenyl- λ^5 -phosphanylidene)acetates from Triphenylphosphine, Acetylenic Esters, and 2-Naphthalenethiol

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A one-pot synthesis of alkyl 2-(2-oxo-1,2-dihydronaphtho[2,1-b]thiophen-1-yl)-2-(1,1,1-triphenyl- λ^5 -phosphanylidene)acetates in fairly high yields by the reaction of 2-naphthalenethiol, dialkyl acetylenedicarboxylates and triphenylphosphine is reported. The formulas of these compounds were confirmed by IR, ¹H,³¹P, and ¹³C NMR spectroscopy. The NMR spectra indicated that solutions of the phosphorus ylides (CDCl₃ as solvent) contain two rotamers (**E** and **Z**). The relative percentages of rotamers in CDCl₃ for each phosphorus ylide were determined from the ³¹P NMR spectra.

Keywords 2-Naphthalenethiol; acetylenic esters; Michael addition; phosphorus ylide; vinyltriphenylphosphonium salt

INTRODUCTION

Phosphorus ylides are important reagents in synthetic organic chemistry,¹⁻¹⁶ especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activity.⁶ 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.^{18–30} Phosphorus ylides are a class of special type of zwitterions, which bear strongly nucleophilic electron rich carbanions. The electron distribution around the P⁺-C⁻ bond and its consequent chemical implications had been probed

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and assessed through theoretical, spectroscopic and crystallographic investigations.³⁰ Proton affinity of these ylides can be used as a molecular guide to assess their utility as synthetic reagents and their function as ligands in coordination and organometallic chemistry.^{17,30} The nucleophilicity at the ylidic carbon is a factor of essential mechanistic importance in the use of these ylides as Wittig reagents. In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts.^{18–28} In this paper, we wish to describe a simple method for the preparation of alkyl 2-(2-oxo-1,2-dihydronaphtho[2,1-b]thiophen-1-yl)-2-(1,1,1-triphenyl- λ^5 -phosphanylidene)acetates from three-component reaction of 2-naphthalenethiol, dialkyl acetylenedicarboxylates and triphenylphosphine in fairly high yields (*Scheme 1*).

RESULTS AND DISCUSSION

The phosphorus ylide (7) may result from initial addition of triphenylphosphine 1 to the acetylenic ester 2 and concomitant protonation of the 1:1 adduct by 2-naphthalenethiol 3 leads to vinyltriphenylphosphonium salts 4, which undergo the Michael addition reaction with conjugate base to produce sterically congested phosphorus ylide (5). The phosphorus ylide 5 convert to the stable phosphorus ylide 7 via organophosphorus intermediate $\mathbf{6}$ in the reaction conditions. TLC indicated formation of ylides 7 in acetone at room temperature. The reaction was completed at room temperature in 2 h. The reaction proceeds smoothly and cleanly under mild conditions and no side reactions were observed. The mechanism of the reaction has not been established experimentally. However, a possible explanation is proposed in Scheme 1. The formulas of the products 7 were deduced from their IR, ¹H NMR, ¹³C NMR, and ¹³P NMR spectra (See Experimental section). The ³¹P NMR spectra indicated that solutions of compound 7 (CDCl₃ as solvent) contain two rotamers (7E and 7Z). The relative percentages of rotamers in CDCl₃ for each ylide **7** were determined from the ³¹P NMR spectra. The IR spectrum of **7a** showed strong adsorptions at 3054 (CH, aromatic), 1739 (C=O, ester), 1592 (C=O, ester), 1439 (C=C), 1262 (CH, aliphatic), 1192 (C-O, ester), and 1123 (C-O, ester) cm⁻¹ indicating the presence of the mentioned groups in its formula. The ¹H NMR spectrum of 7a compound exhibited four signals readily recognized as arising from methoxy group ($\delta = 3.81$ ppm, s), two aliphatic CH groups ($\delta = 4.28$ (d, ${}^{3}J_{HP} =$ 19.3 Hz) and 4.41 (d, ${}^{3}J_{HP} =$ 18.5 Hz) ppm, for two rotamers of the phosphorus ylide) and aromatic moieties ($\delta = 7.2-7.7$ ppm, m). The ¹H decoupled ¹³C NMR spectrum of **7a** showed 16 distinct resonances (52.59 (OCH₃); 125.56, 126.00, 127.24, 127.50, 127.66, 128.59, 131.93,



SCHEME 1 \mathbf{M} = major rotamer and \mathbf{m} = minor rotamer.

131.98, 133.54, 133.74, and 133.89 (CH and C groups)) in agreement with the **7a** formula. Partial assignment of these resonances is given in the spectral analysis section (See Experimental section). The ³¹P NMR spectrum of **7a** exhibited two signals readily recognized as arising from phosphorus atom of P=C groups ($\delta = 22.66$ and 23.06 ppm, **Z** and **E** rotamers). The ¹H, ³¹P, and ¹³C NMR spectra of compound **7b** are similar to those of **7a**, except for the ester groups (¹H and ¹³C NMR), which exhibit characteristic signals with appropriate chemical shifts (see Spectral Analysis section).^{28,31}

CONCLUSION

In summary, we have found a simple and efficient method for the preparation of alkyl 2-(2-oxo-1,2-dihydronaphtho[2,1-b]thiophen-1yl)-2-(1,1,1-triphenyl- λ^5 -phosphanylidene)acetates (7) from the threecomponent reaction of 2-naphthalenethiol, dialkyl acetylenedicarboxylates and triphenylphosphine in fairly high yields. We believe the reported method offers a simple and efficient route for the preparation of the stabilized phosphorus ylides 7 (Scheme 1). Its ease of work-up and fairly good yields make it a useful addition to modern synthetic methodologies.^{28,31} 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 FT-IR Mattson 1000 spectrometer. ¹H, ³¹P and ¹³C NMR spectra were measured with a BRUKER DRX-250 AVANCE spectrometer at 250.00, 101.25, and 62.50 MHz respectively.

General Procedure for the Preparation of Ylides 7a-b

To a magnetically stirred solution of triphenylphosphine 1 (0.262 g, 1.00 mmol) and 2-naphthalenethiol (0.16 g, 1.0 mmol) in acetone (4 ml) was added dropwise a mixture of dialkyl acetylenedicarboxylate (0.13 ml, 1.0 mmol) in acetone (3 ml) at -10° C over 15 min. The mixture was allowed to warm up to room temperature and stirred for 2 h. The volume of solvent in the mixture was reduced (*ca.* up to 3 ml) and white crystals of the product were separated by simple filtration. The crystals were washed with cold acetone (2 ml) and then dried at room temperature (**7a**, white crystals, m.p. 176.8–177.2°C, yield 74.0%; **7b**, white crystals, m.p. 144.7–145.2°C, yield 69.0%). The characterization data of the compounds (**7a–b**) are given below.

Spectral Data for Methyl 2-(2-Oxo-1,2-dihydronaphtho [2,1-b]thiophen-1-yl)-2-(1,1,1-triphenyl- λ^5 -phosphanylidene) acetate 7a

IR (KBr) (v_{max} , cm⁻¹): 3054; 2954; 1739; 1592; 1439; 1262; 1192, and 1123. ¹H NMR, δ_H : 3.81 (3 H, s, OCH₃); 4.28 (1 H, d, ³J_{HP} = 19.3 Hz, major rotamer) and 4.41 (1 H, d, ³J_{HP} = 18.5 Hz, minor rotamer); 7.2–7.7 (21 H, m, arom).¹³C NMR (CDCl₃) δ_C : 52.59 (OCH₃); 125.56, 126.00, 127.24, 127.50, 127.66, 128.59, 131.93, 131.98, 133.54, 133.74,

and 133.89. ³¹P NMR (CDCl₃, major rotamer (M) 59% and minor rotamer (m) 41%), (CDCl₃) δ_P : 22.66 and 23.06.

Spectral Data for Ethyl 2-(2-Oxo-1,2-dihydronaphtho [2,1-b]thiophen-1-yl)-2-(1,1,1-triphenyl- λ^5 -phosphanylidene) acetate 7b

IR (KBr) v_{max} , cm⁻¹): 3054, 2985, 1731, 1592, 1439, 1192, and 1123. ¹H NMR, δ_H : 1.2–1.4 (3 H, m, CH₃); 4.0–4.1 (2 H, m, OCH₂); 4.25 (1 H, d, ³J_{HP} = 14.3 Hz, major rotamer) and 4.43 (1 H, d, ³J_{HP} = 19.0 Hz, minor rotamer); 7.2–7.7 (21 H, m, arom). ¹³C NMR (CDCl₃) δ_C : 14.11 (CH₃); 61.34 (OCH₂); 125.45, 125.91, 127.22, 127.48, 127.55, 127.72, 128.37, 128.54, 129.94, 130.21, 131.83, 131.88, 131.95, 132.01, 132.16, 133.56, 133.78, and 133.94.³¹P NMR (CDCl₃, major rotamer (M) 51% and minor rotamer (m) 49%), δ_P : 22.58 and 22.95.

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