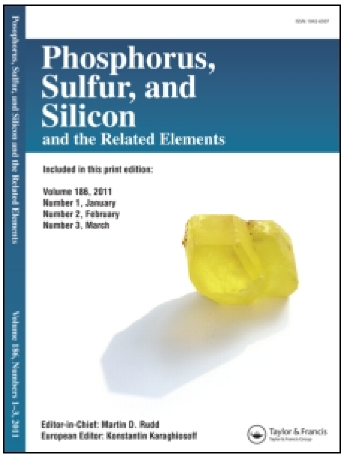


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Issa Amini[a]; Ali Ramazani[b]; Hamideh Ahankar[c]
[a] Chemistry Department, Payam Noor University of Abhar, Abhar, Iran [b] Chemistry Department, Zanjan University, Zanjan, Iran [c] Chemistry Department, Islamic Azad University-Abhar Branch, Abhar, Iran

To cite this Article Amini, Issa , Ramazani, Ali and Ahankar, Hamideh(2008) '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', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 8, 1994 — 1999

To link to this Article: DOI: 10.1080/10426500701839825

URL: http://dx.doi.org/10.1080/10426500701839825

Phosphorus, Sulfur, and Silicon, 183:1994–1999, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701839825

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

Issa Amini,[1] Ali Ramazani,[2] and Hamideh Ahankar[3]
[1]Chemistry Department, Payam Noor University of Abhar, Abhar, Iran
[2]Chemistry Department, Zanjan University, Zanjan, Iran
[3]Chemistry Department, Islamic Azad University-Abhar Branch,
Abhar, Iran

*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,^{31}P, and ^{13}C NMR spectroscopy. The NMR spectra indicated that solutions of the phosphorus ylides ($CDCl_3$ as solvent) contain two rotamers (**E** and **Z**). The relative percentages of rotamers in $CDCl_3$ for each phosphorus ylide were determined from the ^{31}P NMR spectra.*

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

INTRODUCTION

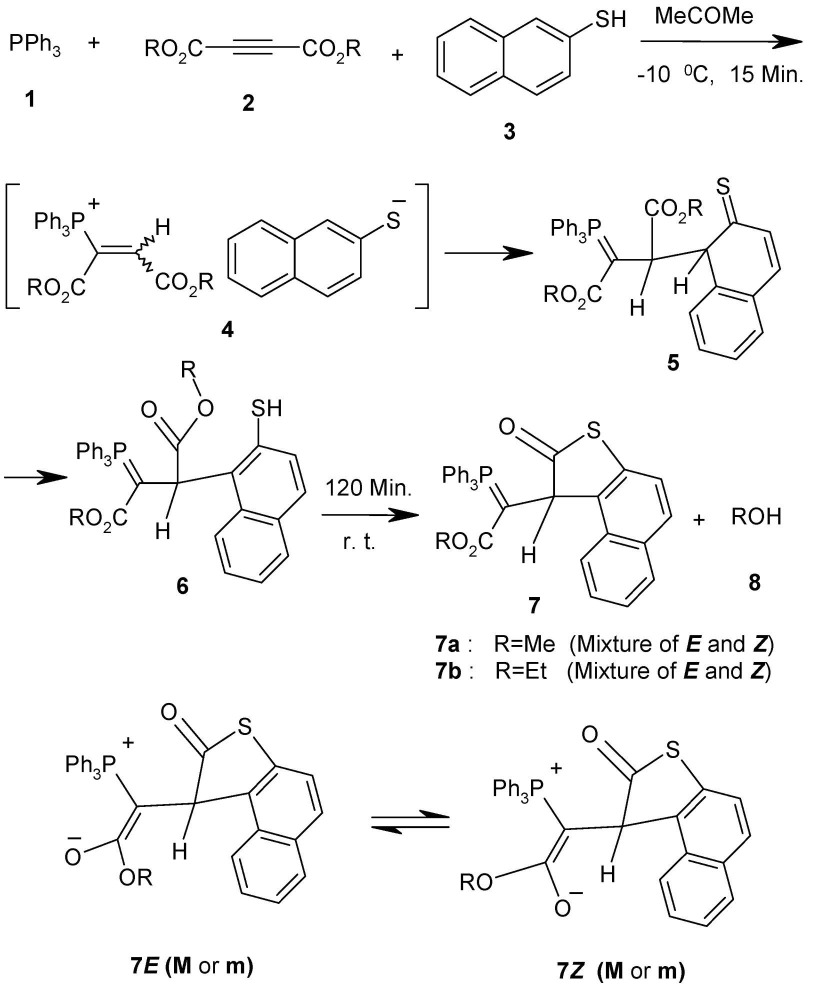
Phosphorus ylides are important reagents in synthetic organic chemistry,[1–16] especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activity.[6] β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of 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

Received 6 September 2007; accepted 13 September 2007.
This work was supported by the Islamic Azad University-Abhar Branch.

Address correspondence to Ali Ramazani, Chemistry Department, Zanjan University, P O Box 45195-313, Zanjan, Iran. E-mail: aliramazani@gmail.com 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 **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, ^{1}H NMR, ^{13}C NMR, and ^{13}P NMR spectra (See Experimental section**).** The ^{31}P NMR spectra indicated that solutions of compound **7** ($CDCl_3$ as solvent) contain two rotamers (**7***E* and **7***Z*). The relative percentages of rotamers in $CDCl_3$ for each ylide **7** were determined from the ^{31}P 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 ^{1}H NMR spectrum of **7a** compound exhibited four signals readily recognized as arising from methoxy group (δ = 3.81 ppm, s), two aliphatic CH groups (δ = 4.28 (d, $^3J_{HP}$ = 19.3 Hz) and 4.41 (d, $^3J_{HP}$ = 18.5 Hz) ppm, for two rotamers of the phosphorus ylide) and aromatic moieties (δ = 7.2–7.7 ppm, m). The ^{1}H decoupled ^{13}C NMR spectrum of **7a** showed 16 distinct resonances (52.59 (OCH_3); 125.56, 126.00, 127.24, 127.50, 127.66, 128.59, 131.93,



SCHEME 1 **M** = major rotamer and **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 ^{31}P NMR spectrum of **7a** exhibited two signals readily recognized as arising from phosphorus atom of P=C groups (δ = 22.66 and 23.06 ppm, ***Z*** and ***E*** rotamers). The ^{1}H, ^{31}P, and ^{13}C NMR spectra of compound **7b** are similar to those of **7a**, except for the ester groups (^{1}H and ^{13}C 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-1-yl)-2-(1,1,1-triphenyl-λ^5-phosphanylidene)acetates **(7)** from the three-component 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. ^{1}H, ^{31}P and ^{13}C 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) ($\upsilon_{\max}$, cm^{-1}): 3054; 2954; 1739; 1592; 1439; 1262; 1192, and 1123. ^{1}H NMR, δ_H : 3.81 (3 H, s, OCH_3); 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).^{13}C NMR ($CDCl_3$) δ_C: 52.59 (OCH_3); 125.56, 126.00, 127.24, 127.50, 127.66, 128.59, 131.93, 131.98, 133.54, 133.74, and 133.89. ^{31}P NMR ($CDCl_3$, major rotamer (M) 59% and minor rotamer (m) 41%), ($CDCl_3$) 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. ^{1}H NMR, δ_H: 1.2–1.4 (3 H, m, CH_3); 4.0–4.1 (2 H, m, OCH_2); 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). ^{13}C NMR ($CDCl_3$)δ_C : 14.11 (CH_3); 61.34 (OCH_2); 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.^{31}P NMR ($CDCl_3$, major rotamer (M) 51% and minor rotamer (m) 49%), δ_P: 22.58 and 22.95.

REFERENCES

[1] O. I. Kolodiazhnyi, *Russ. Chem. Rev*., **66,** 225 (1997).
[2] K. M. Pietrusiewiz and M. Zablocka, *Chem. Rev*., **94,** 1375 (1994).
[3] J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis,* J. I. G. Cadogon, Ed. (Academic Press, New York, 1979).
[4] B. E. Maryanoff and A. B. Reitz, *Chem. Rev*., **89,** 863 (1989).
[5] R. A. Cherkasov and M. A. Pudovik, *Russ. Chem. Rev*., **63,** 1019 (1994).
[6] O. I. Kolodiazhnyi, *Phosphorus Ylides, Chemistry and Application in Organic Synthesis* (Wiley-VCH, New York, 1999).
[7] H. J. Bestmann, *Angew. Chem*., **89,** 361 (1977).
[8] A. W. Johnson, *Ylide Chemistry* (Academic Press, London, 1966).
[9] G. Keglevich, H. Forintos, T. Körtvélyesi, and L. Tőke, *J. Chem. Soc., Perkin Trans. 1*, 26 (2002).
[10] Keglevich, T. Körtvélyesi, H. Forintos, Á. Gy. Vaskó, V. Izvekov, and L. Tőke, *Tetrahedron*, **58,** 372 (2002).
[11] G. Keglevich, T. Körtvélyesi, H. Forintos, and S. Lovas, *J. Chem. Soc. Perkin Trans. 2*, 1645 (2002).
[12] G. Keglevich, H. Forintos, A. Ujvári, T. Imre, K. Ludányi, Z. Nagy and L. Tőke, *J. Chem. Res.*, 432 (2004).
[13] G. Keglevich, T. Körtvélyesi, A. Ujvári, and E. Dudás, *J. Organomet. Chem.,* **690,** 2497 (2005).
[14] G. Keglevich, E. Dudás, M. Sipos, D. Lengyel, and K. Ludányi, *Synthesis,* 1365 (2006).
[15] G. Keglevich, H. Forintos and T. Körtvélyesi, *Current Org. Chem.*, **8,** 1245 (2004).
[16] V. Nair, C. Rajesh, A. U. Vinod, S. Bindu, A. R. Sreekanth, J. S. Mathess, and L. Balagopal, *Acc. Chem. Res*., **36,** 899 (2003).
[17] W. C. Kaska, *Coord. Chem. Rev.,* **48,** 1 (1983).
[18] A. Ramazani, A. Abbasi Motejadded, and E. Ahmadi, *Phosphorus, Sulfur, and Silicon,* **181,** 233 (2006), and references cited therein.
[19] I. Yavari and A. Ramazani, *Synth. Commun.*, **27,** 1449 (1997).
[20] A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41,** 567 (2000).

[21] I. Yavari, A. Ramazani, and A. Yahya-Zadeh, *Synth. Commun.*, **26,** 4495 (1996).
[22] I. Yavari and A. Ramazani, *Phosphorus, Sulfur, and Silicon*, **130,** 73 (1997).
[23] A. Ramazani, A. Momeni-Movahhed, and F. Gouranlou, *Phosphorus, Sulfur, and Silicon,* **177,** 903 (2002).
[24] A. Ramazani, B. Mohammadi, and N. Noshiranzadeh, *Phosphorus, Sulfur, and Silicon,* **178,** 545 (2003).
[25] A. Ramazani, B. Mohammadi, and N. Noshiranzadeh, *Phosphorus, Sulfur, and Silicon,* **178,** 767 (2003).
[26] A. Ramazani, N. Noshiranzadeh, and B. Mohammadi, *Phosphorus, Sulfur, and Silicon,* **178,** 761 (2003).
[27] A. Ramazani, N. Noshiranzadeh, and B. Mohammadi, *Phosphorus, Sulfur, and Silicon,* **178,** 539 (2003).
[28] A. Ramazani and H. Ahani, *Phosphorus, Sulfur, and Silicon,* **170,** 181 (2001).
[29] K. Becker, *Tetrahedron*, **36,** 1717 (1980).
[30] D. E. C. Cobridge, *Phosphorus: An Outline of Chemistry, Biochemistry and Uses* (Elsevier, Amsterdam, 1995), 5th ed.
[31] A. Ramazani, A. R. Kazemizadeh, E. Ahmadi, K. Ślepokura, and T. Lis, *Z. Naturforsch.*, **61b,** 1128 (2006).