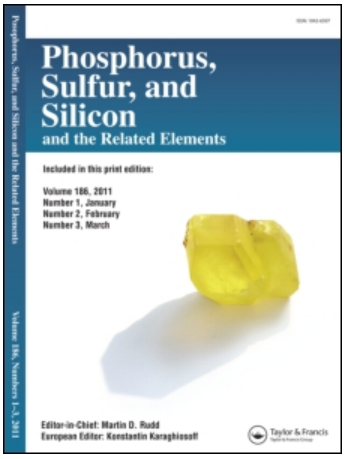

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Facile Synthesis of Stable Phosphorus Ylides Containing Chlorine and Sulfur Derived from 6-Chloro-2-benzoxazolethiol and 2-Chloro-phenothiazine

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To cite this Article Maghsoodlou, Malek Taher , Hazeri, Nourollah , Khorasani, Sayyed Mostafa Habibi , Moghaddam, Hadi Mahmoudi , Nassiri, Mahmoud and Salehzadeh, Jaber(2009) 'A Facile Synthesis of Stable Phosphorus Ylides Containing Chlorine and Sulfur Derived from 6-Chloro-2-benzoxazolethiol and 2-Chloro-phenothiazine', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 7, 1713 — 1721
To link to this Article: DOI: 10.1080/10426500802275093
URL: http://dx.doi.org/10.1080/10426500802275093

Phosphorus, Sulfur, and Silicon, 184:1713–1721, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802275093

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A Facile Synthesis of Stable Phosphorus Ylides Containing Chlorine and Sulfur Derived from 6-Chloro-2-benzoxazolethiol and 2-Chloro-phenothiazine

Malek Taher Maghsoodlou, Nourollah Hazeri, Sayyed Mostafa Habibi Khorasani, Hadi Mahmoudi Moghaddam, Mahmoud Nassiri, and Jaber Salehzadeh
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Stable crystalline phosphorus ylides containing chlorine and sulfur were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylene-dicarboxylates in the presence of 6-chloro-2-benzoxazolethiol and 2-chloro-phenothiazine. These stable ylides exist in solution as a mixture of two geometrical isomers. This is caused by the conjugation of the ylide moiety with the adjacent carbonyl group, which results in a restricted rotation around the respective carbon-carbon bond.

Keywords Acetylenic ester; geometrical isomers; NH-acids; stable phosphorus ylides; triphenylphosphine

INTRODUCTION

The synthesis of phosphorus ylides is important in organic chemistry because of the application of these compounds in the synthesis of organic products,[1–14] especially in the synthesis of naturally occurring products with biological and pharmacological activity.[15–19] Phosphorus ylides are usually prepared by deprotonation of phosphonium salts, which can be obtained by the reaction of triphenylphosphine with an alkyl halide.[1–3] In recent years, a three-component method has been developed[20–30] for the synthesis of organophosphorus compounds using a novel approach that employs vinylphosphonium salts. Here we

Received 17 April 2008; accepted 15 June 2008.
We gratefully acknowledge financial support from the Research Council of the University of Sistan and Baluchestan.
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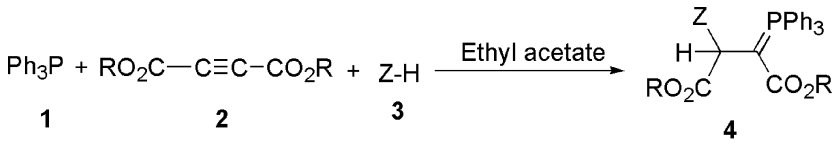
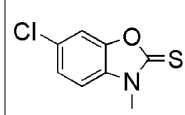
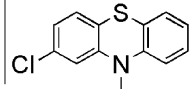
describe an efficient synthetic route to stable phosphorus ylides derived from 6-chloro-2-benzoxazolethiol and 2-chloro-phenothiazine. The benzoxazole and phenothiazine moieties as well as their derivatives are widely used in making medicines.[31,32] Thus, the reaction of triphenylphosphine **1** and dialkyl acetylenedicaboxylates **2** in the presence of compounds **3** leads to the corresponding stable heterocyclic phosphorus ylides **4** in excellent yields (see Scheme 1).



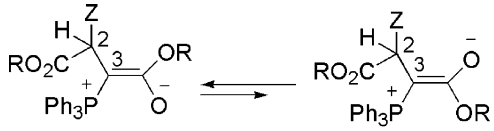
4	Z	R	Yield (%)
a		Me	92
b		Et	90
c		Bu^t	94
d		Me	95
e		Et	91

SCHEME 1

RESULTS AND DISCUSSION

The reaction of 6-chloro-2-benzoxazolethiol and 2-chloro-phenothiazine with dialkyl-acetylenedicarboxylates **2** in the presence of triphenylphosphine **1** proceeded in ethyl acetate as solvent at room temperature and was completed within a few hours. The ^{1}H and ^{13}C NMR spectrum of the crude product clearly indicated the formation of the stable phosphorus ylides **4**. No product other than **4** could be detected by NMR spectroscopy. The structures of compounds **4a–e** were determined from the IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **4a–e** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group resulting in a hindered rotation around the C-C bond connecting these two groups. Interconversion of the geometrical isomers (*E*)-**4** and (*Z*)-**4** is slow on the NMR time scale at ambient temperature (see Scheme 2). Selected ^{1}H, ^{13}C, and ^{31}P NMR

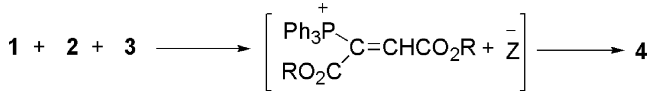
chemical shifts and coupling constants for the major (M) and the minor (m) geometrical isomers of compounds **4a–e** are shown in Table I.



SCHEME 2

As can be seen, only one geometrical isomer was observed for the di-*tert*-butyl derivatives of **4**, presumably, because of the bulky *tert*-butyl groups.

On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[1–3] it is reasonable to assume that the formation of the phosphorus ylides **4** is initiated by the addition of triphenylphosphine to the corresponding acetylenic esters. Protonation of the resulting 1:1 adduct by the acid Z-H followed by addition of the conjugated base Z^- yields the phosphoranes **4** (see Scheme 3).



SCHEME 3

The ^{1}H NMR spectrum of **4a** showed four sharp lines at $\delta = 3.21$, 3.80, 3.81, and 3.83 ppm arising from the methoxy protons. The signal for methine protons appeared as doublet at $\delta = 5.78$ ppm ($^3J_{PH} =$

TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for 2-*H*, OR, CO_2R, C-2, and C-3 in the Major (M) and Minor (m) Isomers of Compounds 4a–e

	Isomer	H-2 ($^3J_{PH}$)	OR	CO_2R	C-2 ($^2J_{PC}$)	C-3 ($^1J_{PC}$)	^{31}P
4a	M	5.78 (17.3)	3.21	3.80	62.8 (17.4)	40.5 (124.0)	23.9
4a	m	5.72 (17.0)	3.81	3.83	63.3 (14.1)	41.9 (131.9)	25.0
4b	M	5.74 (17.8)	3.78	4.25	62.9 (17.5)	40.2 (123.6)	23.9
4b	m	5.57 (19.8)	3.82	4.34	63.2 (5.9)	40.7 (132.2)	25.4
4c	M	5.56 (18.5)	1.00	1.57	63.5 (17.9)	39.6 (123.8)	23.5
4d	M	4.21 (14.6)	3.81	3.96	65.4 (14.7)	41.4 (124.2)	24.5
4d	m	4.14 (16.1)	3.93	3.98	64.8 (14.6)	41.6 (135.5)	23.5
4e	M	4.19[a]	3.44	4.28	65.0 (16.9)	40.3 (123.6)	24.8
4e	m	4.24[a]	3.80	4.44	65.6 (14.9)	41.3 (135.2)	23.5

[a]Broad signal.

17.3 Hz) and 5.72 ppm ($^3J_{PH} = 17.0$ Hz) for the *E* and *Z* isomers, respectively. The ^{13}C NMR spectrum of **4a** displayed 26 distinct resonances in good agreement with the presence of a mixture of the two conformational isomers.

The ^{1}H and ^{13}C NMR spectra of compounds **4b–e** are similar to those of **4a**, except for the signals resulting from the ester group, which are characteristic for the respective substituent R. The structural assignments made for compounds **4a–e** on the basis of the ^{1}H and ^{13}C NMR spectra were supported also by the IR spectra. The carbonyl region of the spectra exhibits absorption bands for each compound. Of special interest is the ester absorption of these compounds at 1731–1612 cm^{-1}. Conjugation with the ylide moiety accounts for the shift of the carbonyl absorption bands to lower wave numbers.

In summary, we have prepared novel phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 6-chloro-2-benzoxazolethiol or 2-chlorophenothiazine. The present method carries the advantage that not only is the reaction performed under neutral conditions, but the substances also can be mixed without any activation or modifications. The 6-chloro-2-benzoxazolethiol and 2-chloro-phenothiazine containing phosphorus ylides **4a–e** may be considered as potentially useful synthetic intermediates. The procedure described here might be employed as a general method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained with a Bruker DRX-300 Avance instrument in $CDCl_3$ as solvent at 300.1, 75.4, and 121.5 MHz, respectively. The mass spectra were measured with a GCMS-QP 5050A mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates, triphenlphosphine, 6-chloro-2-benzoxazolethiol, and 2-chloro-phenothiazine were purchased from Fluka, and were used without further purification.

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and 6-chloro-2-benzoxazolethiol (1 mmol) or 2-chlorophenothiazine (1 mmol) in 10 mL of dry ethyl acetate, a solution of the

corresponding acetylenedicarboxylate (1 mmol) in 4 mL of dry ethyl acetate was added dropwise over a period of 10 min. After approximately 6 h of stirring at room temperature, the product was filtered and washed with cold diethyl ether (3 × 5 mL).

Dimethyl-2-(6-chloro-2-benzoxazolethiol-*N*-yl)-3-(triphenylphosphanylidene)-butanedioate (*4a*)

Colorless crystals; mp: 162–164°C; yield: 0.54 g (92%). IR (KBr) (ν_{max}, cm^{-1}): 1728, 1617 (C=O). MS (m/z, %): 471 (M-2CO2Me, 31), 408 (M-C_7H_3ClNOS, 22), 262 (PPh_3, 100), 183 (PPh_2, 94), 108 (PPh, 43), 77 (Ph, 16). Anal. Calcd. for $C_{31}H_{25}ClNO_5PS$ (590.0): C, 63.10; H, 4.27; N, 2.37%. Found: C, 63.33; H, 4.48; N, 2.29%.

Major Isomer (72%): ^{1}H NMR ($CDCl_3$): $\delta = 3.21$ (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 5.78 (d, $^3J_{PH} = 17.3$ Hz, 1H, P=C-C*H*), 7.28–7.86 (m, 18H, arom-*H*). ^{13}C NMR ($CDCl_3$): $\delta = 40.5$ (d, $^1J_{PC} = 124.0$ Hz, P=C), 49.6 (CH_3), 52.3 (CH_3), 62.8 (d, $^2J_{PC} = 17.4$ Hz, P=C-*CH*), 110.2, 114.2, 124.9, 125.6 (d, $^1J_{PC} = 92.0$ Hz, C-*i*), 129.2 (d, $^3J_{PC} = 12.7$ Hz, C-*m*), 129.8, 132.0, 132.6 (C-*p*), 133.4 (d, $^2J_{PC} = 9.7$ Hz, C-*o*), 147.2, 169.9 (d, $^3J_{PC} = 11.4$ Hz, C=O ester), 170.0 (d, $^2J_{PC} = 11.3$ Hz, P-C=C), 180.0 (C=S). ^{31}P NMR ($CDCl_3$): $\delta = 23.9$.

Minor Isomer (28%): ^{1}H NMR ($CDCl_3$): $\delta = 3.81$, (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 5.72 (d, $^3J_{PH} = 17.0$ Hz, 1H, P=C-C*H*), 6.88–7.86 (m, 18H, arom-*H*). ^{13}C NMR ($CDCl_3$): $\delta = 40.9$ (d, $^1J_{PC} = 131.9$ Hz, P=C), 53.0 (CH_3), 53.6 (CH_3), 63.3 (d, $^2J_{PC} = 14.1$ Hz, P=C-*CH*), 110.5, 113.3, 124.5 124.9 (d, $^1J_{PC} = 92.0$ Hz, C-*i*), 125.5, 129.2 (d, $^3J_{PC} = 12.7$ Hz, C-*m*), 130.0, 132.2, 132.6 (C-*p*), 133.5 (d, $^2J_{PC} = 8.6$ Hz, C-*o*), 147.4, 169.6 (d, $^3J_{PC} = 13.9$ Hz, C=O), 170.4 (d, $^2J_{PC} = 12.9$ Hz, P-C= *C*), 180.3 (C=S). ^{31}P NMR ($CDCl_3$): $\delta = 25.0$.

Diethyl-2-(6-chloro-2-benzoxazolethiol-*N*-yl)-3-(triphenylphosphanylidene)-butanedioate (*4b*)

White solid; mp: 149–151°C; yield: 0.56 g (90%). IR (KBr) (ν_{max}, cm^{-1}): 1731, 1620 (C=O). MS (m/z, %): 433 (M-PPh_2, 21), 282 (M-PPh_2 and CO_2Et, 38), 262 (PPh_3, 100), 183 (PPh_2, 83), 108 (PPh, 44), 77 (Ph, 9). Anal. Calcd. for $C_{33}H_{29}ClNO_5PS$ (618.1): C, 64.13; H, 4.73; N, 2.27%. Found: C, 64.27; H, 4.79; N, 2.11%.

Major Isomer (78%): ^{1}H NMR ($CDCl_3$): $\delta = 0.49$ (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3), 1.29 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_2), 3.76–3.80 (m, ABX_3 system, CH_2), 4.16–4.34 (m, ABX_3 system, CH_2), 5.74 (d, $^3J_{PH} = 17.8$ Hz, 1H, P=C-*CH*), 7.27–7.90 (m, 18H, arom-*H*). ^{13}C NMR ($CDCl_3$): $\delta = 14.0$

(CH_3), 14.2 (CH_3), 40.2 (d, $^1J_{PC}$ = 123.6 Hz, P=C), 58.4 (CH_2), 61.8 (CH_2), 62.9 (d, $^2J_{PC}$ = 17.5 Hz, P=C-*C*H), 110.2, 114.3, 124.8, 125.8 (d, $^1J_{PC}$ = 92.0 Hz, C-*i*), 129.1 (d, $^3J_{PC}$ = 12.2 Hz, C-*m*), 129.9, 132.0, 132.5 (d, $^4J_{PC}$ = 2.3 Hz, C-*p*), 133.5 (d, $^2J_{PC}$ = 9.7 Hz, C-*o*), 147.2, 169.2 (d, $^3J_{PC}$ = 13.2 Hz, C=O), 169.5 (d, $^2J_{PC}$ = 12.4 Hz, P-C= *C*), 180.1 (C=S).^{31}P NMR ($CDCl_3$): δ = 23.9.

Minor Isomer (22%): ^{1}H NMR ($CDCl_3$): δ = 1.21 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.34 (t, $^3J_{HH}$ = 7.1 Hz, CH_3), 3.75–3.82 (m, ABX_3 system, CH_2), 4.30–4.40 (m, ABX_3 system, CH_2), 5.57 (d, $^3J_{PH}$ = 19.8 Hz, 1H, P=C-C*H*), 6.85–7.90 (m, 18H, arom-*H*). ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 14.8 (CH_3), 40.7 (d, $^1J_{PC}$ = 132.2 Hz, P=C), 61.3 (CH_2), 61.7 (CH_2), 63.2 (d, $^2J_{PC}$ = 5.9 Hz, P=C-*C*H), 110.5, 113.4, 124.3, 125.2 (d,$^1J_{PC}$ = 92.4 Hz, C-*i*), 128.5 (d, $^3J_{PC}$ = 12.2 Hz, C-*m*), 130.1, 132.1, 132.5 (d, $^4J_{PC}$ = 2.3 Hz, C-*p*), 133.5 (d, $^2J_{PC}$ = 9.7 Hz, C-*o*), 147.4, 169.5 (d, $^3J_{PC}$ = 13.6 Hz, C=O), 170.0 (d, $^2J_{PC}$ = 17.8 Hz, C=O), 180.4 (C=S).^{31}P NMR ($CDCl_3$): δ = 25.4.

Di-*tert*-buthyl-2-(6-chloro-2-benzoxazolethiol-*N*-yl)-3-(tri-phenylphosphanylidene)-butanedioate (*4c*)

White solid; mp: 161–163°C; yield: 0.63 g (94%). IR (KBr) (υ_{max}, cm^{-1}): 1725, 1613 (C=O). MS (m/z, %): 572 (M-CO_2CMe_3, 32), 377 (M-C_7H_3ClNOS and 2 CMe_3, 42), 288 (M-PPh_2 and 2 CO_2CMe_3, 25), 262 (PPh_3, 100), 183 (PPh_2, 63), 108 (PPh, 33), 57 (CMe_3, 57). Anal. Calcd. for $C_{37}H_{37}ClNO_5PS$ (674.2): C, 65.92; H, 5.53; N, 2.08%. Found: C, 66.07; H, 5.72; N, 2.03%.

^{1}H NMR ($CDCl_3$): δ = 1.00 (s, 9H, CH_3), 1.57 (s, 9H, CH_3), 5.56 (d, $^3J_{PH}$ = 18.5 Hz, 1H, P=C-*CH*), 7.24–8.40 (m, 18H, arom-*H*). ^{13}C NMR ($CDCl_3$): δ = 28.1 (CH_3), 28.3 (CH_3), 39.6 (d, $^1J_{PC}$ = 123.8 Hz, P=C), 63.5 (d, $^2J_{PC}$ = 17.9 Hz, P=C-*CH*), 78.0 (*C*Me_3), 81.7 (*C*Me_3), 110.0, 114.3, 124.7, 126.2 (d, $^1J_{PC}$ = 91.7 Hz, C-*i*), 128.9 (d, $^3J_{PC}$ = 12.2 Hz, C_{-m}), 130.0, 132.0, 132.4 (d, $^4J_{PC}$ = 2.2 Hz, C-*p*), 133.5 (d, $^2J_{PC}$ = 9.7 Hz, C-*o*), 147.2, 167.7 (d, $^3J_{PC}$ = 13.1 Hz, C=O), 169.0 (d, $^2J_{PC}$ = 11.8 Hz, P-C= *C*), 180.2 (C=S). ^{31}P NMR ($CDCl_3$): δ = 23.5.

Dimethyl-2-(2-chloro-phenothiazine-*N*-yl)-3-(triphenyl-phosphanylidene)-butanedioate (*4d*)

Yellow powder; mp: 134–136°C; yield: 0.61 g (95%). IR (KBr) (υ_{max}, cm^{-1}): 1735, 1629 (C=O). MS (m/z, %): 519 (M-2CO_2Me, 25), 345 (M-PPh_3 and OCH_3, 23), 262 (PPh_3, 100), 183 (PPh_2, 97), 108 (PPh, 43),

77 (Ph, 23). Anal. Calcd. for $C_{36}H_{29}ClNO_4PS$ (638.1): C, 67.76; H, 4.58; N, 2.20%. Found: C, 67.80; H, 4.65; N, 2.18%.

Major Isomer (54%): ^{1}H NMR ($CDCl_3$): $\delta = 3.81$ (s, 3H, CH_3), 3.96 (s, 3H, CH_3), 4.21 (d, $^3J_{PH} = 14.6$ Hz, 1H, P=C-*CH*), 6.65–7.72 (m, 22H, arom-*H*). ^{13}C NMR ($CDCl_3$): $\delta = 41.4$ (d, $^1J_{PC} = 124.2$ Hz, P= *C*), 49.1 (CH_3), 52.8 (CH_3), 65.4 (d, $^2J_{PC} = 14.7$ Hz, P=C-*CH*), 113.3, 114.6, 115.1, 120.1, 122.2, 124.0, 126.4 (d, $^1J_{PC} = 92.0$ Hz, C-*i*), 126.1, 126.4, 126.9, 128.5 (d, $^3J_{PC} = 12.3$ Hz, C-*m*), 131.8 (d, $^4J_{PC} = 2.7$ Hz, C-*p*), 132.0, 132.1, 132.61, 133.4 (d, $^2J_{PC} = 9.7$ Hz, C-*o*), 169.0 (d, $^3J_{PC} = 13.2$ Hz, C=O), 173.6 (d, $^2J_{PC} = 17.6$ Hz, P-C= *C*).^{31}P NMR ($CDCl_3$): $\delta =$ 24.5.

Minor Isomer (46%): ^{1}H NMR ($CDCl_3$): $\delta = 3.93$ (s, 3H, CH_3), 3.98 (s, 3H, CH_3), 4.14 (d, $^3J_{PH} = 16.1$ Hz, 1H, P=C-*CH*), 6.65-7.72 (m, 22H, arom-*H*). ^{13}C NMR ($CDCl_3$): $\delta = 41.6$ (d, $^1J_{PC} = 135.5$ Hz, P= *C*), 52.6 (CH_3), 52.9 (CH_3), 64.8 (d, $^2J_{PC} = 14.6$ Hz, P=C-*CH*), 113.3, 114.6, 115.1, 120.1, 122.2, 124.0, 125.2 (d, $^1J_{PC} = 91.8$ Hz, C-*i*), 126.2, 126.5, 127.0, 128.5 (d, $^3J_{PC} = 12.2$ Hz, C-*m*), 131.8 (d, $^4J_{PC} = 2.7$ Hz, C-*p*), 132.1, 132.2, 132.7, 133.5 (d, $^2J_{PC} = 9.8$ Hz, C-*o*), 168.9 (d, $^3J_{PC} = 13.5$ Hz, C=O), 173.8 (d, $^2J_{PC} = 16.8$ Hz, C=O). ^{31}P NMR ($CDCl_3$): $\delta = 23.5$.

Diethyl-2-(2-chloro-phenothiazine-*N*-yl)-3-(triphenyl-phosphanylidene)-butanedioate (*4e*)

White powder; mp: 153–155°C; yield: 0.61 g (91%). IR (KBr) (υ_{max}, cm^{-1}): 1722, 1612 (C=O). MS (*m/z*, %):MS (m/z, %): 520 (M-$2CO_2Et$, 26), 440 (M-$C_{12}H_7ClNS$, 19), 359 (M-PPh_3 and OEt, 31), 262 (PPh_3, 100), 183 (PPh_2, 97), 108 (PPh, 48), 77 (Ph, 17). Anal. Calcd. for $C_{38}H_{33}ClNO_4PS$ (666.2): C, 68.51; H, 4.99; N, 2.10%. Found: C, 68.64; H, 5.13; N, 2.06%.

Major Isomer (60%): ^{1}H NMR ($CDCl_3$): $\delta = 0.43$ (broad, 3H, CH_3), 1.32 (broad, 3H, CH_3), 3.44 (broad, 2H, CH_2), 4.19 (broad, 1H, P=C-*CH*), 4.28 (broad, 2H, CH_2), 6.66–7.96 (m, 22H, arom-*H*). ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3), 14.3 (CH_3), 40.3 (d, $^1J_{PC} = 123.6$ Hz, P=*C*), 57.7 (CH_2), 61.3 (CH_2), 65.0 (d, $^2J_{PC} = 16.9$ Hz, P=C-*CH*), 113.5, 114.7, 115.2, 121.5, 121.6, 122.4, 125.6, 126.0, 126.3, 126.8 (d, $^1J_{PC} = 92.4$ Hz, C-*i*), 128.4 (d, $^3J_{PC} = 11.7$ Hz, C-*m*), 131.7 (d, $^4J_{PC} = 2.7$ Hz, C-*p*), 132.0, 132.1, 132.6, 133.5 (d, $^2J_{PC} = 9.7$ Hz, C-*o*), 168.2 (d, $^3J_{PC} =$ 13.3 Hz, P-C=*C*), 172.9 (d, $^2J_{PC} = 12.4$ Hz, C=O).^{31}P NMR ($CDCl_3$): $\delta =$ 24.8.

Minor Isomer (40%): ^{1}H NMR ($CDCl_3$): $\delta = 1.34$ (broad, 6H, CH_3), 3.80 (broad, 2H, CH_2), 4.24 (broad, 1H, P=C-*CH*), 4.44 (broad, 2H, CH_2), 6.66–7.96 (m, 22H, arom-*H*).^{13}C NMR ($CDCl_3$): $\delta = 13.9$ (CH_3),

14.0 (CH_3), 41.3 (d, $^1J_{PC} = 135.2$ Hz, P=*C*), 60.9 (CH_2), 61.3 (CH_2), 65.6 (d, $^2J_{PC} = 14.9$ Hz, P=C-*CH*), 113.4, 114.5, 115.3, 121.4, 121.7, 122.4, 125.5, 126.2, 126.4, 126.6 (d, $^1J_{PC} = 92.3$ Hz, C-*i*), 128.4 (d, $^3J_{PC} = 12.5$ Hz, C-*m*), 131.7 (d, $^4J_{PC} = 2.7$ Hz, C-*p*), 132.0, 132.1, 132.7, 133.5 (d, $^2J_{PC} = 9.7$ Hz, C-*o*), 168.7 (d, $^3J_{PC} = 12.6$ Hz, C=O), 173.4 (d, $^2J_{PC} = 13.1$ Hz, P-C= *C*). ^{31}P NMR ($CDCl_3$): $\delta = 23.5$.

REFERENCES

[1] H. R. Hudson, In *Chemistry of Organophosphorus Compounds, Vol. 1. Primary, Secondary and Tertiary Phosphines and Heterocyclic Organophosphorus III Compounds*, F. R. Hantley, Ed., (Wiley, New York, 1990).
[2] R. Engel, *Synthesis of Carbon-Phosphorus Bonds* (CRC Press, Boca Raton, 1988).
[3] J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis* (Academic Press, New York, 1979).
[4] M. T. Maghsoodlou, N. Hazeri, S. M. Habibi-Khorassani, R. Kakaei, and M. Nassiri, *Phosphorus, Sulfur, and Silicon*, **181,** 25 (2006).
[5] Z. Hassani, M. R. Islami, H. Sheibani, M. Kalantari, and K. Saidi, *Arkivoc*, **i,** 89 (2006).
[6] I. Yavari, H. Djahaniani, M. T. Maghsoodlou, and N. Hazeri, *J. Chem. Res.* (S), 382 (1998).
[7] I. Yavari, M. Bayat, M. T. Maghsoodlou, and N. Hazeri, *Phosphorus, Sulfur, and Silicon*, **177,** 2599 (2002).
[8] M. T. Maghsoodlou, N. Hazeri, S. M. Habibi-Khorassani, G. Afshari, and M. Nassiri, *J. Chem. Res.*, 727 (2005).
[9] I. Yavari and M. Adib, *Tetrahedron*, **57,** 5873 (2001).
[10] A. A. Esmaeili, M. R. Islami, and G. R. Kardan-Moghaddam, *Phosphorus, Sulfur, and Silicon*, **181,** 527 (2006).
[11] I. Yavari and L. Ahmadian-Razlighi, *Phosphorus, Sulfur, and Silicon*, **181,** 771 (2006).
[12] M. Adib and M. H. Sayahi, *Monatsh. Chem.*, **137,** 207 (2006).
[13] M. T. Maghsoodlou, N. Hazeri, S. M. Habibi-Khorassani, M. Nassiri, G. Marandi, A. Ghulame Shahzadeh, and H. R. Bijanzadeh, *Phosphorus, Sulfur, and Silicon*, **181,** 1117 (2006).
[14] M. T. Maghsoodlou, N. Hazeri, S. M. Habibi-Khorassani, R. Kakaei, and M. Nassiri, *Phosphorus, Sulfur, and Silicon*, **181,** 25 (2006).
[15] M. T. Maghsoodlou, S. M. Habibi-Khorassani, N. Hazeri, M.Nassiri, R. Kakaei, and G. Marandi, *Phosphorus, Sulfur, and Silicon*, **181,** 553 (2006).
[16] M. T. Maghsoodlou, S. M. Habibi-Khorassani, N. Hazeri, M. Nassiri, G. Marandi, G. Afshari, and U. Niroumand, *Sulfur Chem.*, **26,** 261 (2005).
[17] I. Yavari and F. Feiz-Javadian, *Phosphorus, Sulfur, and Silicon*, **181,** 1011 (2006).
[18] M. R. Islami, F. Mollazehi, A. Badiei, and H. Sheibani, *Arkivoc*, **xv,** 25 (2005).
[19] M. Kalantari, M. R. Islami, Z. Hassani, and K. Saidi, *Arkivoc*, **x,** 55 (2006).
[20] I. Yavari and M. R. Islami, *J. Chem. Res.* (S), 166 (1998).
[21] I .Yavari and E. Karimi, *Phosphorus, Sulfur, and Silicon*, **182,** 595 (2007).
[22] I. Yavari and S. Asghari, *Tetrahedron*, **55,** 11853 (1999).
[23] M. R. Islami, Z. Hassani, H. Sheibani, B. Abdolahzadeh, and N. Etminan, *Tetrahedron*, **59,** 4993 (2003).

[24] M. T. Maghsoodlou, R. Heydari, S. M. Habibi-Khorassani, M. K. Rofouei, M. Nassiri, E. Mosaddegh, and A. Hassankhani, *Sulfur Chem.*, **27,** 341 (2006).
[25] M. T. Maghsoodlou, S. M. Habibi-Khorassani, M. K. Rofouei, S. R. Adhamdoust, and M. Nassiri, *Arkivoc*, **xii,** 145 (2006).
[26] M. T. Maghsoodlou, N. Hazeri, S. M. Habibi-Khorassani, L. Saghatforoush, M. K. Rofouei, and M. Rezaie, *Arkivoc*, **xiii,** 117 (2006).
[27] I. Yavari, M. R. Islami, and H. R. Bijanzadeh, *Tetrahedron*, **55,** 5547 (1999).
[28] I. Yavari and M. T. Maghsoodlou, *Tetrahedron Lett.*, **39,** 4579 (1998).
[29] I. Yavari, F. Nasiri, and H. Djahaniani, *Phosphorus, Sulfur, and Silicon*, **178,** 2627 (2003).
[30] A. Shaabani, M. B. Teimouri, I. Yavari, H. Norouzi Arasi, and H. R. Bijanzadeh, *J. Fluorine Chem.*, **103,** 155 (2000).
[31] T. L. Gilchrist, *Heterocyclic Chemistry* (Wiley, New York, 1985).
[32] H. J. Roth and A. Kleemann, *Pharmaceutical Chemistry* (Ellis Horwood, London, 1988).