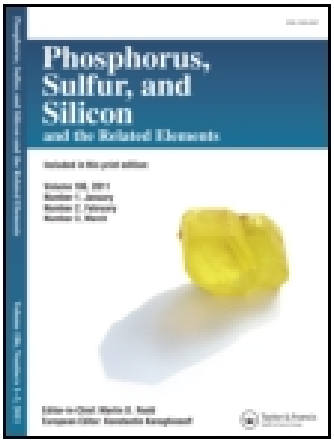


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Solvent Effects on the Chemoselectivity of Stable Phosphorus Ylides Involving a Sulfonamide

Reza Heydari [a], Nourallah Hazeri [a], Malek Taher Maghsoodlou [a], Sayyed Mostafa Habibi Khorassani [a], Ghasem Marandi [b], Nariman Maleki [a], Roya Kabiri [c] & Bahram Gholipour Soleymani [a]

[a] Chemistry Department, The University of Sistan and Baluchestan, Zahedan, Iran

[b] Department of Chemistry, Faculty of Science, Payame Noor University of Khoy, Khoy, Iran

[c] Faculty of Chemistry, The University of Tabriz, Tabriz, Iran

Published online: 24 Sep 2010.

To cite this article: Reza Heydari, Nourallah Hazeri, Malek Taher Maghsoodlou, Sayyed Mostafa Habibi Khorassani, Ghasem Marandi, Nariman Maleki, Roya Kabiri & Bahram Gholipour Soleymani (2010) Solvent Effects on the Chemoselectivity of Stable Phosphorus Ylides Involving a Sulfonamide, Phosphorus, Sulfur, and Silicon and the Related Elements, 185:10, 2135-2141, DOI: 10.1080/10426500903530883

To link to this article: http://dx.doi.org/10.1080/10426500903530883

Phosphorus, Sulfur, and Silicon, 185:2135–2141, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903530883

SOLVENT EFFECTS ON THE CHEMOSELECTIVITY OF STABLE PHOSPHORUS YLIDES INVOLVING A SULFONAMIDE

Reza Heydari,[1] Nourallah Hazeri,[1] Malek Taher Maghsoodlou,[1] Sayyed Mostafa Habibi Khorassani,[1] Ghasem Marandi,[2] Nariman Maleki,[1] Roya Kabiri,[3] and Bahram Gholipour Soleymani[1]

[1]*Chemistry Department, The University of Sistan and Baluchestan, Zahedan, Iran*
[2]*Department of Chemistry, Faculty of Science, Payame Noor University of Khoy, Khoy, Iran*
[3]*Faculty of Chemistry, The University of Tabriz, Tabriz, Iran*

Hydrazine sulfonamide derivatives undergo a smooth reaction with dialkyl acetylenedicarboxylates in the presence of triphenylphosphine in varieties of solvent for generation of phosphorus ylides in a chemoselective manner.

Keywords Acetylenic diesters; chemoselective reaction; hydrazine sulfonamide; phosphorus ylides; sulfonamide; triphenylphosphine

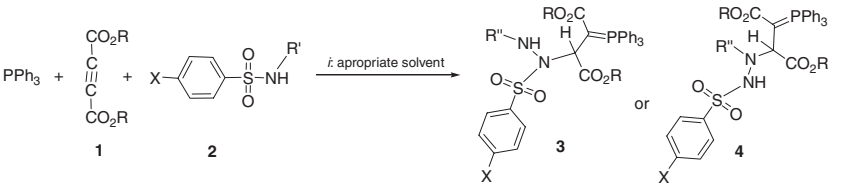
INTRODUCTION

Sulfonamide derivatives have a great potential as pharmacological and agricultural agents due to their biological properties.[1–4] The impact of organophosphorus chemistry on modern synthetic chemistry is difficult to quantify, but one can safely assume that the study of this element has influenced all area of chemical endeavor.[5–9] Synthesis of phosphonium salts often occurs by reaction between triphenylphosphine and an alkyl halide in the presence of a base, but more recently, there are many reports that triphenylphosphine and acetylenic esters are used for generation of stable phosphonium ylides.[5–17] We describe in this article an efficient synthetic route for synthesis of stable phosphorus ylides containing sulfonamide in the presence of various solvents. Solvent selection in organic synthesis is one of the major routes for approaching goals. For this reason, the effects of various solvents on the chemoselectivity of stable phosphorus were investigated in the current work.

RESULTS AND DISCUSSION

This report contains the results of the reaction between triphenylphosphine and sulfonamides **2**, which leads to stable phosphorus ylides **3** and **4** in 89–95% yields (see

Received 2 August 2009; accepted 27 November 2009.
We gratefully acknowledge financial support from the Research Council of the University of Sistan & Baluchestan.
Address correspondence to Malek Taher Maghsoodlou, Chemistry Department, The University of Sistan and Baluchestan, P. O. Box 98135-674, Zahedan, Iran. E-mail: mt_maghsoodlou@yahoo.com



2	R	R'	X	Solvent	Selectvity (%) of **3** and **4**	
a	Me	NH_2	Me	ether	66	34
				ethyl acetate	6	94
b	Et	NH_2	H	acetonitrile	----	single product
c	Me	PhNH	H	10 : 1 ether / acetone	single product	----
d	*t*-butyl	PhNH	H	ether	single product	----

Scheme 1

Scheme 1). In continuation of our research on the development of synthesic routes of heterocyclic and organophosphorus compounds,[18–20] we describe in this article the effects of solvents on the chemoselectivity of new ylides **3** and **4**. Compounds **3** and **4** are stable solids whose structures are fully characterized and supported by elemental analyses and spectroscopic data.

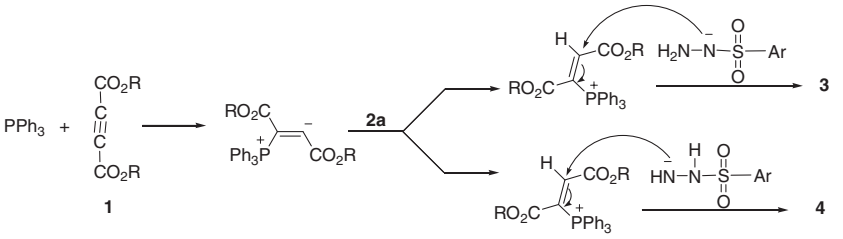
The ^{1}H NMR spectrum of **3a** exhibited single sharp lines arising from methyl (δ = 2.41 ppm), methoxycarbonyl groups (δ = 3.10 and 3.55 ppm), a broad singlet from $SO_2NN\mathit{H}_2$ (δ = 4.11 ppm), and a doublet from methine proton (δ = 4.94 ppm, J = 17.0 Hz), respectively. Aromatic protons of **3a** resonated at δ = 7.22–7.75 ppm for the major diasteroisomer. The ^{13}C NMR spectrum of compound **3a** showed carbonyl groups at δ = 170.70 ppm, J = 7.5 Hz and δ = 172.36 ppm, J = 13.8 Hz, respectively. Other partial spectroscopic information is reported in the Experimental section for the minor diasteroisomer.

The ^{1}H NMR spectrum of **4a** displayed single sharp lines arising from methyl (δ = 2.46 ppm), methoxycarbonyl groups (δ = 3.07 and 3.74 ppm), a doublet from methine proton (δ = 4.61 ppm, J = 8.3 Hz), a doublet from $SO_2HNN\mathit{H}$ (δ = 3.61 ppm, J = 9.3 Hz), and a doublet from $SO_2\mathit{H}NNH$ (δ = 6.62 ppm, J = 2.7 Hz), respectively. Aromatic protons of **4a** resonated in δ = 7.25–7.75 ppm for the major diasteroisomer. The ^{13}C NMR spectrum of compound **4a** showed characteristic carbonyl groups at δ = 169.75 ppm, J = 11.5 Hz and δ = 173.32 ppm, J = 11.3 Hz, respectively. Other partial spectroscopic information is available in the Experimental section for the minor diasteroisomer.

The mass spectra of compounds **3a** and **4a** displayed molecular ion peaks at appropriate *m/z* values.

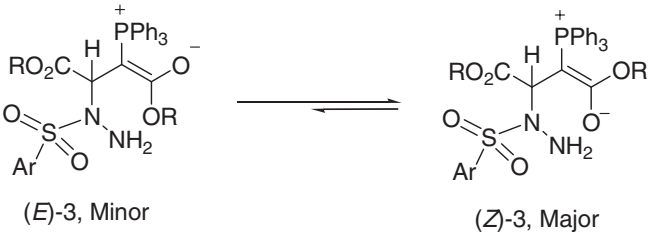
On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[5–13] it is reasonable to assume that phosphorus ylides **3** and **4** result from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-compounds to form phosphoranes **3** and **4** (see Scheme 2).

The ylides **3** and **4** exist in solution as two geometrical isomers (*Z*) and (*E*) because the negative charge of the ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group. Rotation around the carbon–carbon double bond is slow on



Scheme 2

the NMR time scale for interconversion process between both (*Z*)- and (*E*)- geometrical isomers at ambient temperature (Scheme 3). Due to the sheer difficulty of the separation in the mixture of both geometrical isomers (*Z*) and (*E*) from each other in solution, preparation of a single crystal is impossible.



Scheme 3

In conclusion, the reaction between triphenylphosphine and acetylenic esters in the presence of NH-compounds such as sulfonamides provides a simple, one-pot, and efficient entry for the synthesis of stable, sulfonamide-containing ylides with probable pharmacological properties. The present method carries the advantages involving generation of different products in the presence of various solvent media, neutral conditions, and possible mixture of substances without any prior activation and modification.

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-500 Avance instrument using $CDCl_3$ as applied solvent TMS as internal standard at 500.1, 125.8, and 202.4 MHz, respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. In addition, the mass spectra were recorded on a Shimadzu GC/MS QP 5050 mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates and triphenylphosphine were purchased from Fluka and were used without further purification. All sulfonamides have been prepared by known procedures.[21]

General Procedures for Preparation of Stable Phosphorus Ylides 3 or 4

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and NH compound **2** (1 mmol) in diethyl ether (10 mL), a mixture of dimethyl acetylenedicarboxylates (0.14 g,1 mmol) in diethyl ether (3 mL) was added dropwise over 10 min at ambient temperature. After the appropriate time (4–12 h) stirring at ambient temperature, the product was filtered off and recrystallized from ethyl acetate.

Dimethyl 2-(Para-toluenesulfonamido-*N*-amino-*N*-yl)-3-(triphenylphosphoranylidene)butandioate (3a)

Yellow powder, yield: 0.54 g (92%), mp 136–139 °C. IR (KBr) (λ_{max}, cm^{-1}): 3422 and 3315 (NH_2), 1733 and 1630 (2 C=O_{ester}), 1319 and 1144 (SO_2). MS (*m/z*,%): 590 (M^+, 1), 573 (2), 456 (2), 417 (1), 392 (4), 333 (17), 262 (56), 183 (100), 157 (26), 108 (48), 91 (53). Anal Calcd for $C_{31}H_{31}N_2O_6PS$ (590.63): C, 63.04; H, 5.29; N, 4.74%; Found: C, 63.22; H, 5.17; N, 4.61%.

***Major isomer* (*Z*)-3a** (65%): ^{1}H NMR: 2.41 (3H, s, Me), 3.10 and 3.55 (6H, 2s, 2 OCH_3), 4.11 (2H, br s, NH_2), 4.94 (1H, d, $^3J_{HP}$ = 17.0 Hz, P=C−C*H*), 7.22 (2H, d, $^3J_{HH}$ = 8.1 Hz, CH_{aryl}), 7.28 (2H, d, $^3J_{HH}$ = 8.1 Hz, CH_{aryl}), 7.54–7.75 (15H, m, 3 C_6H_5). ^{13}C NMR: 21.48 (s, Me), 41.13 (d, $^1J_{PC}$ = 125.8 Hz, P=*C*−CH), 48.90 and 49.15 (2s, 2 OCH_3), 62.25 (d, $^2J_{PC}$ = 15.5 Hz, P=C−*C*H), 126.46 (d, $^1J_{PC}$ = 92.3 Hz, C_{ipso} of 3 C_6H_5), 128.13 and 128.70 (2s, 4 CH_{aryl}), 128.9 (d, $^3J_{PC}$ = 15.5 Hz, C_{meta} of 3 C_6H_5), 129.30 (s, C_{aryl}), 132.24 (C_{para} of 3 C_6H_5), 133.74 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho} of 3 C_6H_5), 143.30 (s, C_{aryl}), 170.70 (d, $^2J_{PC}$ = 7.5 Hz, C=O_{ester}), 172.36 (d, $^3J_{PC}$ = 13.8 Hz, C=O_{ester}). ^{31}P NMR: 23.18 (Ph_3P^+-C).

***Minor isomer* (*E*)-3a** (35%): ^{1}H NMR: 2.47 (3H, s, Me), 3.43 and 3.71 (6H, 2s, 2 OCH_3), 3.93 (2H, br s, NH_2), 5.00 (1H, d, $^3J_{HP}$ = 16.4 Hz, P=C−C*H*), 7.21–7.23 (4H, m, 4 CH_{aryl}), 7.54–7.82 (15H, m, 3 C_6H_5). ^{13}C NMR: 21.54 (s, Me), 41.83 (d, $^1J_{PC}$ = 123.7 Hz, P=*C*−CH), 49.17 and 50.02 (2s, 2 OCH_3), 62.17 (d, $^2J_{PC}$ = 14.7 Hz, P=C−*C*H), 126.79 (d, $^1J_{PC}$ = 91.5 Hz, C_{ipso} of 3 C_6H_5), 128.42 and 128.80 (2s, 4 CH_{aryl}), 129.01 (d, $^3J_{PC}$ = 12.3 Hz, C_{meta} of 3 C_6H_5), 129.30 (s, C_{aryl}), 132.22 (C_{para} of 3 C_6H_5), 133.74 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho} of 3 C_6H_5), 142.38 (s, C_{aryl}), 169.13 (d, $^2J_{PC}$ = 7.3 Hz, C=O_{ester}), 172.14 (d, $^3J_{PC}$ = 12.9 Hz, C=O_{ester}). ^{31}P NMR: 24.71 (Ph_3P^+-C).

Dimethyl 2-(Para-toluenehydrazidsulfonamido-*N*-yl)-3-(triphenylphosphoranylidene)butandioate (4a)

Yellow powder, yield: 0.56 g (95%), mp 153–156 °C. IR (KBr) (λ_{max}, cm^{-1}): 3370 and 3262 (2 NH), 1732 and 1680 (2 C=O_{ester}), 1330 and 1127 (SO_2). MS (*m/z*,%): 590 (M^+, 2), 575 (3), 406 (2), 390 (3), 347 (17), 262 (91), 183 (100), 108 (44), 91 (62). Anal Calcd for $C_{31}H_{31}N_2O_6PS$ (590.63): C, 63.04; H, 5.29; N, 4.74%; Found: C, 62.98; H, 5.21; N, 4.83%.

***Major isomer* (*Z*)-4a** (68%): ^{1}H NMR: 2.46 (3H, s, Me), 3.07 and 3.74 (6H, 2s, 2 OCH_3), 3.61 (1H, m, P=C−C*H*), 4.61 (1H, br d, $^3J_{HH}$ = 8.3 Hz, SO_2HNN*H*), 6.62 (1H, d, *J* = 2.7 Hz, SO_2*H*NNH), 7.25–7.75 (20H, m, 3 C_6H_5 and 4 CH_{aryl}). ^{13}C NMR: 21.53 (s, Me), 41.33 (d, $^1J_{PC}$ = 124.7 Hz, P=*C*−CH), 48.89 and 52.04 (2s, 2 OCH_3), 63.71 (d, $^2J_{PC}$ = 15.6 Hz, P=C−*C*H), 126.71 (d, $^1J_{PC}$ = 92.7 Hz, C_{ipso} of 3 C_6H_5), 128.13 and 128.70 (2s, 4 CH_{aryl}), 128.7 (d, $^3J_{PC}$ = 12.1 Hz, C_{meta} of 3 C_6H_5), 132.08 (C_{para} of 3 C_6H_5), 133.75

(d, $^2J_{PC}$ = 9.4 Hz, C_{ortho} of 3 C_6H_5), 133.79 and 143.29 (2s, 2 C_{aryl}), 169.75 (d, $^3J_{PC}$ = 11.5 Hz, C=O_{ester}), 173.32 (d, $^2J_{PC}$ = 11.3 Hz, C=O_{ester}). ^{31}P NMR: 23.25 (Ph_3P^+-C).

Minor isomer **(*E*)-4a** (32%):^{1}H NMR: 2.40 (3H, s, Me), 3.44 and 3.70 (6H, 2s, 2 OCH_3), 3.55 (1H, m, P=C−C*H*), 4.39 (1H, br d, $^3J_{HH}$ = 9.7 Hz, SO_2HNN*H*), 6.62 (1H, d, *J* = 2.7 Hz, SO_2*H*NNH), 7.25–7.83 (20H, m, 3 C_6H_5 and 4 CH_{aryl}). ^{13}C NMR: 21.53 (s, Me), 41.73 (d, $^1J_{PC}$ = 125.1 Hz, P=*C*−CH), 49.86 and 51.92 (2s, 2 OCH_3), 63.11 (d, $^2J_{PC}$ = 15.3 Hz, P=C−*C*H), 126.94 (d, $^1J_{PC}$ = 91.8 Hz, C_{ipso} of 3 C_6H_5), 128.17 (s, 2 CH_{aryl}), 128.91 (d, $^3J_{PC}$ = 12.3 Hz, C_{meta} of 3 C_6H_5), 129.30 (s, 2 CH_{aryl}), 132.23 (C_{para} of 3 C_6H_5), 133.75 (d, $^2J_{PC}$ = 9.4 Hz, C_{ortho} of 3 C_6H_5), 135.67 and 142.80 (2s, 2 C_{aryl}), 169.13 (d, $^3J_{PC}$ = 12.1 Hz, C=O_{ester}), 173.51 (d, $^2J_{PC}$ = 11.8 Hz, C=O_{ester}). ^{31}P NMR: 23.74 (Ph_3P^+-C).

Diethyl 2-(Benzenehydrazidsulfonamido-*N*-yl)-3-(triphenylphosphoranylidene)butandioate (4b)

Yellow powder, yield: 0.55 g (91%), mp 152–154 °C. IR (KBr) (λ_{max}, cm^{-1}): 3323 and 3270 (2 NH), 1732 and 1657 (2 C=O_{ester}), 1330 and 1127 (SO_2). MS (*m*/*z*,%): 604 (M^+, 2), 573 (8), 531 (23), 502 (7), 374 (48), 262 (73), 183 (100), 108 (53), 156 (25). Anal Calcd for $C_{32}H_{33}N_2O_6PS$ (604.65): C, 63.56; H, 5.50; N, 4.63%; Found: C, 63.48; H, 5.63; N, 4.52%.

Major isomer **(*Z*)-4b** (70%): ^{1}H NMR: 0.42 (3H, t, *J* = 6.7 Hz, OCH_2CH_3), 1.28 (3H, t, *J* = 6.4 Hz, OCH_2CH_3), 3.54–3.59 (2H, m, OCH_2CH_3), 3.60–3.64 (2H, m, OCH_2CH_3), 3.84 (1H, br s, P=C−C*H*), 4.70 (1H, br d, $^3J_{HH}$ = 9.8 Hz, SO_2HNN*H*), 6.72 (1H, br s, SO_2*H*NNH), 7.46–7.83 (20H, m, 3 C_6H_5 and 4 CH_{aryl}). ^{13}C NMR: 13.89 and 14.28 (2s, 2 OCH_2CH_3), 41.77 (d, $^1J_{PC}$ = 125.8 Hz, P=*C*−CH), 57.54 and 60.78 (2s, 2 OCH_2CH_3), 63.60 (d, $^2J_{PC}$ = 14.6 Hz, P=C−*C*H), 126.93 (d, $^1J_{PC}$ = 92.0 Hz, C_{ipso} of 3 C_6H_5), 128.11 and 128.64 (2s, 4 CH_{aryl}), 128.70 (d, $^3J_{PC}$ = 12.6 Hz, C_{meta} of 3 C_6H_5), 131.93 (C_{para} of 3 C_6H_5), 132.54 (s, C_{aryl}), 133.79 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho} of 3 C_6H_5), 138.79 (s, C_{aryl}), 169.35 (d, $^3J_{PC}$ = 11.7 Hz, C=O_{ester}), 174.80 (d, $^2J_{PC}$ = 11.1 Hz, C=O_{ester}). ^{31}P NMR: 23.11 (Ph_3P^+-C).

Minor isomer **(*E*)-4b** (30%): ^{1}H NMR: 1.06 (3H, t, *J* = 6.8 Hz, OCH_2CH_3), 1.28 (3H, t, *J* = 6.4 Hz, OCH_2CH_3), 4.00 (1H, br s, P=C−C*H*), 4.07–4.19 (2H, m, OCH_2CH_3), 4.23–4.29 (2H, m, OCH_2CH_3), 4.57 (1H, br d, $^3J_{HH}$ = 10.0 Hz, SO_2HNN*H*), 6.72 (1H, br s, SO_2*H*NNH), 7.46–7.91 (20H, m, 3 C_6H_5 and 4 CH_{aryl}). ^{13}C NMR: 14.28 and 14.87 (2s, 2 OCH_2CH_3), 41.98 (d, $^1J_{PC}$ = 124.97 Hz, P=*C*−CH), 57.99 and 60.78 (2s, 2 OCH_2CH_3), 62.82 (d, $^2J_{PC}$ = 14.8 Hz, P=C−*C*H), 128.15 (d, $^1J_{PC}$ = 91.7 Hz, C_{ipso} of 3 C_6H_5), 128.24 and 128.46 (2s, 4 CH_{aryl}), 128.49 (d, $^3J_{PC}$ = 12.5 Hz, C_{meta} of 3 C_6H_5), 129.11(s, C_{aryl}), 132.00 (C_{para} of 3 C_6H_5), 133.15 (s, C_{aryl}), 134.01 (d, $^2J_{PC}$ = 10.5 Hz, C_{ortho} of 3 C_6H_5), 169.27 (d, $^3J_{PC}$ = 11.5 Hz, C=O_{ester}), 174.92 (d, $^2J_{PC}$ = 11.7 Hz, C=O_{ester}). ^{31}P NMR: 23.67 (Ph_3P^+-C).

Dimethyl 2-(Benzenesulfonamido-*N*-aniline-*N*-yl)-3-(triphenylphosphoranylidene)butandioate (3c)

Pale white powder, yield: 0.52 g (92%), mp 142–145 °C. IR (KBr) (λ_{max}, cm^{-1}): 3414 (NH), 1746 and 1619 (2 C=O_{ester}), 1345 and 1151 (SO_2). MS (*m*/*z*,%): 562 (M^+, 1), 545 (32), 277 (63), 183 (22), 173 (34), 108 (15), 77 (100), 57 (14), 51 (44). Anal Calcd for $C_{36}H_{33}N_2O_6PS$ (652.70): C, 66.25; H, 5.10; N, 4.29%; Found: C, 66.15; H, 5.19; N, 4.13%.

Major isomer **(*Z*)-3c** (77%): ^{1}H NMR: 2.95 and 3.31 (6H, 2s, 2 OCH_3), 4.84 (1H, d, $^{3}J_{HP}$ = 18.0 Hz, P=C−C*H*), 6.58 (1H, s, SO_2NNH), 7.09–7.75 (25H, m, 5 C_6H_5). ^{13}C NMR: 49.08 and 51.68 (2s, 2 OCH_3), 42.13 (d, $^{1}J_{PC}$ = 127.3 Hz, P=*C*−CH), 64.20 (d, $^{2}J_{PC}$ = 16.5 Hz, P=C−*C*H), 114.53 (s, 2 C_{aryl}), 120.28 (s, 1 C_{aryl}), 128.31 (d, $^{1}J_{PC}$ = 97.2 Hz, C_{ipso} of 3 C_6H_5), 128.73 (d, $^{3}J_{PC}$ = 12.2 Hz, C_{meta} of 3 C_6H_5),128.91 (s, 2 C_{aryl}), 131.96 (C_{para} of 3 C_6H_5), 149.58 (s, 1 C_{aryl}), 125.41 (s, 2 C_{aryl}), 132.38 (s, 1 C_{aryl}), 133.70 (d, $^{2}J_{PC}$ = 9.9 Hz, C_{ortho} of 3 C_6H_5), 133.87 (s, 2 C_{aryl}), 138.76 (s, 1 C_{aryl}), 170.26 (d, $^{3}J_{PC}$ = 12.3 Hz, C=O_{ester}), 172.28 (d, $^{2}J_{PC}$ = 12.6 Hz, C=O_{ester}). ^{31}P NMR: 25.26 (Ph_3P^+-C).

Minor isomer **(*E*)-3c** (23%):^{1}H NMR: 3.43 and 3.51 (6H, 2s, 2 OCH_3), 4.99 (1H, d, $^{3}J_{HP}$ = 19.6 Hz, P=C−C*H*), 6.30 (1H, s, SO_2NNH), 6.90–7.75 (25H, m, 5 C_6H_5). ^{13}C NMR: 50.13 and 51.96 (2s, 2 OCH_3), 41.65 (d, $^{1}J_{PC}$ = 128.11 Hz, P=*C*−CH), 63.17 (d, $^{2}J_{PC}$ = 16.3 Hz, P=C−*C*H), 111.83 (s, 2 C_{aryl}), 120.09 (s, 1 C_{aryl}), 126.17 (s, 2 C_{aryl}), 126.24 (d, $^{1}J_{PC}$ = 91.8 Hz, C_{ipso} of 3 C_6H_5), 128.82 (d, $^{3}J_{PC}$ = 11.9 Hz, C_{meta} of 3 C_6H_5), 132.06 (C_{para} of 3 C_6H_5), 133.61 (s, 2 C_{aryl}), 133.80 (d, $^{2}J_{PC}$ = 9.7 Hz, C_{ortho} of 3 C_6H_5), 138.12 (s, 1 C_{aryl}), 148.83 (s, 1 C_{aryl}), 169.13 (d, $^{3}J_{PC}$ = 131.1 Hz, C=O_{ester}), 172.13 (d, $^{2}J_{PC}$ = 12.6 Hz, C=O_{ester}). ^{31}P NMR: 26.11 (Ph_3P^+-C).

Di-*tert*-butyl 2-(Benzenesulfonamido-*N*-aniline-*N*-yl)-3-(triphenylphosphoranylidene)butandioate (3d)

White powder, yield: 0.66 g (89%), mp 137–140 °C. IR (KBr) (λ_{max}, cm^{-1}): 3342 (NH), 1732 and 1639 (2 C=O_{ester}), 1343 and 1164 (SO_2). MS (*m*/*z*,%): 738 (M^+, 2), 601 (9), 573 (24), 371 (11), 262 (49), 183 (56), 108 (27), 91 (100). Anal Calcd for $C_{42}H_{45}N_2O_6PS$ (736.86): C, 68.46; H, 6.16; N, 3.80%; Found: C, 68.57; H, 6.21; N, 3.86%.

Major isomer **(*Z*)-3d**: ^{1}H NMR: 079 and 1.44 (18H, 2s, 2 OC*Me*$_3$), 4.69 (1H, d, $^{3}J_{HP}$ = 18.8 Hz, P=C−C*H*), 6.81 (1H, s, SO_2NNH), 6.96–7.75 (25H, m, 5 C_6H_5). ^{13}C NMR: 28.15 and 28.25 (2s, 2 OC*Me*$_3$), 40.50 (d, $^{1}J_{PC}$ = 125.7 Hz, P=*C*−CH), 64.66 (d, $^{2}J_{PC}$ = 18.0 Hz, P=C−*C*H), 77.42 and 80.85 (2s, 2 O*C*Me$_3$), 114.68 (s, 2 C_{aryl}), 119.90 (s, 1 C_{aryl}), 126.60 (s, 2 C_{aryl}), 128.02 (d, $^{1}J_{PC}$ = 90.4 Hz, C_{ipso} of 3 C_6H_5), 128.53 (d, $^{3}J_{PC}$ = 12.3 Hz, C_{meta} of 3 C_6H_5), 128.92 (s, 2 C_{aryl}), 129.26 (s, C_{aryl}), 131.70 (C_{para} of 3 C_6H_5), 131.88 (s, 2 C_{aryl}), 133.87 (d, $^{2}J_{PC}$ = 9.8 Hz, C_{ortho} of 3 C_6H_5), 138.59 (s, 1 C_{aryl}), 149.83 (s, 1 C_{aryl}), 168.95 (d, $^{3}J_{PC}$ = 12.5 Hz, C=O_{ester}), 170.23 (d, $^{2}J_{PC}$ = 12.4 Hz, C=O_{ester}). ^{31}P NMR: 23.91 (Ph_3P^+-C).

REFRENCES

1. A. Dömling, *Chem. Rev.*, **106,** 17 (2006).
2. C. P. Decicco, J. L. Seng, K. E. Kennedy, M. B. Covington, P. K. Welch, E. C. Arner, R. L. Magolda, and D. J. Nelson, *Bioorg. Med. Chem. Lett.*, **7,** 2331 (1997).
3. A. K. Ghosh, J. F. Kincaid, W. Cho, D. E. Waiters, K. Krishnan, K. A. Hussain, Y. Koo, C. Rudall, L. Holland, and J. Buthod, *Bioorg. Med. Chem. Lett.*, **8,** 687 (1998).
4. W. R. Roush, J. Cheng, B. Knapp-Reed, A. Alvarez-Hernandez, J. H. McKerrow, E. Hansell, and J. C. Engle, *Bioorg. Med. Chem. Lett.*, **11,** 2759 (2001).
5. D. E. C. Corbridge, In *Topics in Phosphorus Chemistry*; M. Grayson and J. Griffith, eds. (Interscience, New York, 1969), vol. 6, pp. 235–365.
6. O. I. Kolodiazhnyi, *Phosphorus Ylides* (Wiley-VCH, Weinheim, Germany, 1999).
7. R. Engel and J. I. Cohen, *Synthesis of Carbon-Phosphorus Bonds*, 2nd ed. (CRC Press, Boca Raton, FL, 2004), chapters 1–3.

8. H. R. Hudson, In *The Chemistry of Organophosphorus Compounds, Vol. 1. Primary, Secondary, and Tertiary Phosphates and Heterocyclic Organophosphorus (III) Compounds*, F. R. Hartley, ed. (Wiley, New York, 1990), pp. 382–472.
9. P. J. Murphy, *Organophosphorus Reagents* (Oxford University Press, Oxford, UK, 2004), Chapters 1 and 2.
10. I. Yavari and K. Karimi, *Phosphorus, Sulfur, and Silicon*, **182,** 595 (2007).
11. M. T. Maghsoodlou, S. M. Habibi-Khorassani, R. Heydari, A. Hassankhani, G. Marandi, M. Nassiri, and E. Mosaddeg, *Mol Divers.*, **11,** 87 (2007).
12. M. T. Maghsoodlou, N. Hazeri, N. S. M. Habibi-Khorassani, R. Heydari, M. Nassiri, G. Marandi, Z. Moeeni, U. Niromand, and Z. Eskandari-Torbaghan, *Phosphorus, Sulfur, and Silicon*, **181,** 865 (2006).
13. S. M. Habibi-Khorassani, M. T. Maghsoodlou, A. Ebrahimi, M. Zakarianejad, and M. Fattahi, *J. Solution Chem.*, **36,** 1117 (2007).
14. S. M. Habibi-Khorassani, M. T. Maghsoodlou, A. Ebrahimi, H. Roohi, M. Zakarianejad, and M. Moradian, *Prog. React. Kinet. Mech.*, **30,** 127 (2005).
15. S. M. Habibi-Khorassani, M. T. Maghsoodlou, M. Zakarianejad, M. A. Kazemian, M. Nassiri, and P. Karimi, *Heteroatom. Chem.*, **19,** 723 (2008).
16. I. Yavari, N. Zabarjad-Shiraz, M. T. Maghsoodlou, and N. Hazeri, *Phosphorus, Sulfur, and Silicon*, **177,** 759 (2002).
17. I. Yavari, N. Zabarjad-Shiraz, and H. R. Bijanzadeh, *Phosphorus, Sulfur, and Silicon*, **179,** 1381 (2004).
18. M. T. Maghsoodlou, L. Saghatforoush, A. Aminkhani, G. Marandi, and R. Kabiri, *J. Sulfur. Chem.*, **27,** 583 (2006).
19. N. Hazeri, S. M. Habibi-Khorassani, M. T. Maghsoodlou, G. Marandi, M. Nassiri, and A. G. Shahzadeh, *J. Chem. Res. (S)*, 215 (2006).
20. M. T. Maghsoodlou, N. Hazeri, M. Nassiri, G. Marandi, A. G. Shahzadeh, and H. R. Bijanzadeh, *Phosphorus, Sulfur, and Silicon*, **181,** 1117 (2006).
21. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell, In *Vogel's Text Book of Practical Organic Chemistry*, 5th ed. (Wiley, New York, 1989), chapter 6, p. 879.