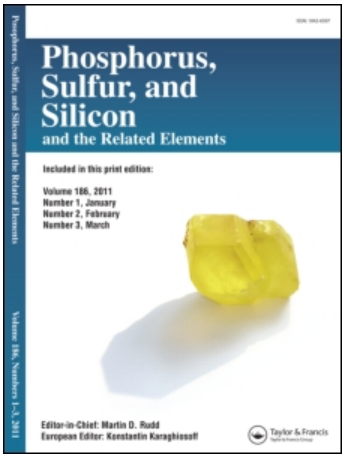

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Three-Component Reaction for an Efficient Synthesis of Stable Phosphorus Ylides Using Mercapto Compounds

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Three-Component Reaction for an Efficient Synthesis of Stable Phosphorus Ylides Using Mercapto Compounds

Zahra Hassani,[1,2] Mohammad Reza Islami,[1] Arman Moradi,[1] and Moazameh Yazdi Rouh-Alamini[1]
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Stabilized phosphorus ylides were obtained from the three-component reaction between dialkyl acetylenedicarboxylate and sulfur compounds such as pyridine-2-thione, 2-furylmethanethiol, ethanedithioamide, and N-phenyl-1,2,4-triazole-3-thiol in the presence of triphenylphosphine in excellent yields.

Keywords Acetylenic ester; ethanedithioamide; 2-furylmethanethiol; phosphorus ylides; pyridine-2-thione; three-component reaction

INTRODUCTION

The development of simple synthetic routes for widely used organic compounds from readily available reagents is one of the goals in organic chemistry.[1] Organophosphorus compounds are synthetic targets of interest, because of their applications in a variety of industrial, biological, and pharmacological activities and chemical synthetic uses.[2–8]

It has been shown that some of heterocyclic compounds exhibit bioactive properties. For example, 2-furylmethanethiol derivatives are found to be novel antitumor compounds.[9] In addition, volatile compounds containing sulfur atoms are a major food aroma class found in vegetables, cooked meat, and other processed foods. These compounds are ubiquitous in animals and plants, and mercapto compounds have been detected in various heated foods.[10–13] There are several reports about furans with a thio group in the literature that possessed meat-like

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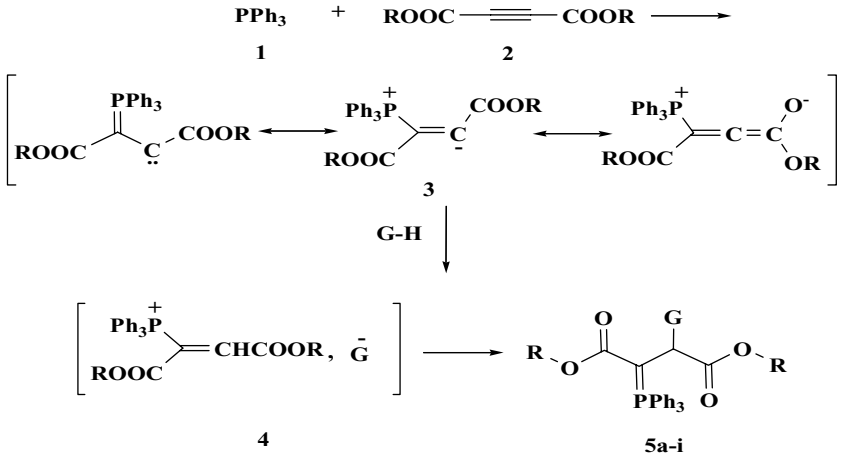
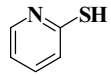
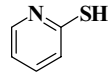
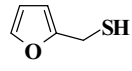
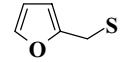
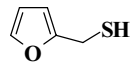
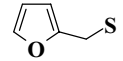
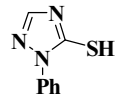
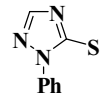
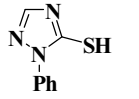
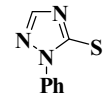
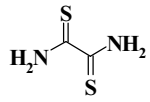
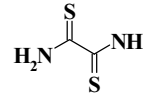
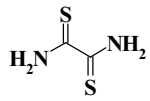
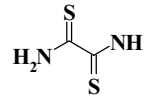
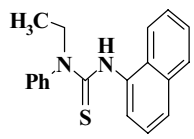
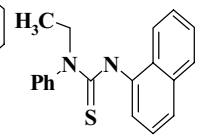
aromas, and the corresponding disulfides that were formed by oxidation of furan thiols were also found to have meat-like characteristics and exceptionally low odor threshold values.[14]

2-Mercaptopyridine can exist in two isomers. These isomers are called thione and thiol tautomers. The pyridine-2-thione (HpyS), which contains the –N(H)-C(=S) chromophore, is a useful model compound for sulfur-containing analogues of purine and pyrimidine bases, and in view of its potential biochemical implications, the coordination chemistry of HpyS and its derivatives has been investigated, particularly during the past decade.[15,16] On the other hand, pyridine-2-thione is able to act as an enzyme inhibitor of the polyphenoloxidase, which is responsible for browning in fruits and vegetables.[17,18] This compound has also been examined as cholesterol biosynthesis inhibitor and studied as a neurotropic agent. This compound also was examined in routine neuropharmacological tests to characterize its activity spectrum and to reveal the influence of the structure on activity, which may indicate further steps in psychotropic drug design.[19] Dithiooxamide, frequently called rubeanic acid, is well-known as a complexing agent. This compound is theoretically capable of participating in complexing as a ligand as well as acting as one of the ligand synthons in template synthesis gelatin-immobilized matrix, and it has been recognized as a reagent for the photometric analysis of nickel and copper.[20–22]

In this article, we wish to describe an efficient conversion of sulfur compounds to a system containing a ylide moiety along with ester groups using the reaction of dialkyl acetylenedicarboxylate, triphenylphosphine, and a desired sulfur compound (Scheme 1).



SCHEME 1 (Continued)

Compound	R	G-H	G	Yield (%)
5a	Me			95
5b	Et			83
5c	Me			90
5d	Et			82
5e	Me			95
5f	Et			98
5g	Me			95
5h	Me			90
5i	Me			76

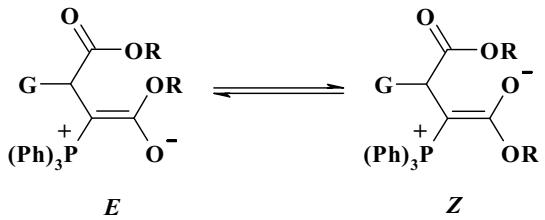
SCHEME 1 (Continued)

RESULTS AND DISCUSSION

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[23–26] it is reasonable to assume that the reaction starts with the Michael addition of triphenylphosphine **1** to electron-deficient acetylenic ester **2** to form the zwitterionic intermediate **3**,[8,27–29] which is subsequently protonated by the sulfur compounds (G-H) to give

vinyltriphenylphosphonium cation **4**. Then, the addition of the conjugate base of the sulfur compounds produces phosphorus ylides **5a–i**.

The produced structures **5a–i** were identified by IR, ^{1}H, and ^{13}C NMR spectra. The ^{1}H NMR and ^{13}C NMR spectral data of new ylides **5a–i** exhibited a mixture of two conformational isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group, and the rotation about the partial double bond in **E**, **Z** geometrical isomers is low on the NMR time scale at ambient temperature (Scheme 2). Conformational isomers in phosphoranes have been previously established and reported in the literature.[30–32]



SCHEME 2

The ^{1}H NMR spectrum of **5a** displayed two sharp lines ($\delta = 3.58$ and 3.66 ppm) for the major isomer arising from the methoxy groups, along with a signal for the methine proton at 5.09 ppm, which appeared as a doublet ($^3J_{PH} = 19.9$ Hz). The corresponding signals for the minor isomer appeared at ($\delta = 3.13$ and 3.74 ppm) for the methoxy groups and at ($\delta = 5.6$ ppm, $^3J_{PH} = 20.9$ Hz) for the methine proton. The ^{13}C NMR spectrum of **5a** displayed signals in agreement with the mixture of two geometrical isomers of *Z* and *E*. Although the presence of the ^{31}P nucleus has complicated both the ^{1}H and ^{13}C NMR spectra of **5a**, it helps in the assignment of signals by long range spin–spin couplings with ^{1}H and ^{13}C nuclei (see the Experimental section). The ^{1}H and ^{13}C NMR spectra of compound **5b** are similar to those of **5a**, except for the ester groups, which exhibited characteristic resonances with appropriate chemical shifts. The ^{1}H NMR and ^{13}C NMR spectral data for compound **5c–i** are consistent with the geometrical isomers (see the Experimental section).

In summary, phosphorus ylides may be prepared by a simple, one-pot, three-component reaction of acetylenic esters, sulfur compounds, and triphenylphosphine. The present method carries the advantage that not only is the reaction performed under neutral conditions, but also that the substances can be mixed without any activation or modification. It seems that the procedure described here may be employed as

an acceptable method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points were obtained on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 Avance (^{1}H at 500 MHz, and ^{13}C at 125.77 MHz). Elemental analysis for C, H, and N were determined by Tarbiat Moallem University using a Heracus CHN-O-Rapid analyzer. All common reagents and solvents were used as obtained from commercial suppliers without further purification. Throughout this section, an asterisk (*) denotes for two rotamers.

Dimethyl 2-(2-Pyridylsulfanyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5a) General Procedure

At ambient temperature, 0.24 mL dimethyl acetylenedicarboxylate (2 mmol) was added dropwise to a stirred solution of 0.53 g triphenylphosphine (2 mmol) and 0.22 g pyridine-2-thione (2 mmol) in a mixture of 10 mL hexane-ethyl acetate (1:2). After the addition was complete (approximately 30 min), the mixture was stirred for an additional 1 h and was subsequently filtered. The solid collected in the filter was washed thoroughly with ethyl acetate to give a yellow powder.

Yellow powder, 0.98 g, mp 152–154°C yield 95%; IR (KBr) (ν_{max}, cm^1) 1741 and 1641(C=O). Major isomer (*E*) (73.25%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.58$ and 3.66 (6H, 2s, 2 CH_3), 5.09 (1H, d, $^{3}J_{PH}$ =19.1 Hz, P=C-CH), 6.44–7.89 (38H, m, arom)*ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 43.71$ (d, $^{1}J_{PC} = 134.4$ Hz, P=C), 49.08 and 52.58 (2 OCH_3), 48.62 (d, $^{2}J_{PC}$ =15.2 Hz, P=C-CH), 118.38 (CH), 121.24 (CH), 127.02 (d, $^{1}J_{PC}$ = 89.9 Hz, C^{ipso}), 129.12 (d,$^{3}J_{PC}$ = 12.4 Hz, CH^{meta}), 131.85 (d, $^{4}J_{PC}$ = 2.6 Hz, CH^{para}), 133.78 (d, $^{2}J_{PC}$ = 9.9 Hz, CH^{ortho}), 135.22 (CH), 148.61 (CH), 160.12 (C), 170.57 (d, $^{2}J_{PC}$ = 13.9 Hz, C=O)*, 173.26 (d, $^{3}J_{PC}$ = 9.5 Hz, C=O)*ppm. Minor isomer (*Z*) (26.75%) ^{1}H NMR (500 MHz, $CDCl_3$):$\delta = 3.13$ and 3.74 (6H, 2s, 2 CH_3), 5.14 (1H, d, $^{3}J_{PH} = 20.9$ Hz, P=C-CH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 42.24$ (d, $^{1}J_{PC} = 137.8$ Hz, P=C), 49.09 and 50.25 (2 OCH_3), 49.30 (d, $^{2}J_{PC}$ =16.3 Hz, P=C-CH), 112.48 (CH), 121.60 (CH), 126.29(d, $^{1}J_{PC} = 91.9$ Hz, C^{ipso}), 128.62 (d,$^{3}J_{PC}$ = 11.9 Hz, CH^{meta}), 132.44 (d, $^{4}J_{PC}$ = 2.8 Hz, CH^{para}), 133.15 (CH), 133.42 (d, $^{2}J_{PC}$ = 9.9 Hz, CH^{ortho}), 148.60 (CH), 159.74 (C) ppm.

Diethyl 2-(2-Pyridylsulfanyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5b)

Yellow powder, 0.90 g, mp 108–110°C yield 83%; IR (KBr) (ν_{max}, cm^1) 1741 and 1641(C=O). Major isomer (*Z*) (58.16%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.43$ (3H, t, $^3J_{HH} = 7.0$ Hz, CH_3), 1.17 (3H, t,$^3J_{HH=}$7.0 Hz, CH_3), 3.69–4.29 (8H, m, OCH_2)*, 5.05 (1H, d, $^3J_{PH}$ =19.2 Hz, P=C-CH), 6.42–7.89 (38H, m, arom)* ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.16$ and 14.17 (2 CH_3), 42.46 (d, $^1J_{PC} = 138.2$ Hz, P=C), 49.58 (d, $^2J_{PC}$ =14.6 Hz, P=C-CH), 61.17 and 61.43 (2 OCH_2), 118.27 (CH), 121.60 (CH), 127.21 (d, $^1J_{PC} = 90.6$ Hz, C^{ipso}), 129.03 (d, $^3J_{PC} = 12.3$ Hz, CH^{meta}), 131.79 (d, $^4J_{PC} = 2.5$ Hz, CH^{para}), 133.79 (d, $^2J_{PC} = 9.9$ Hz, CH^{ortho}), 135.15 (CH), 148.46 (CH), 160.39(C), 170.28 (d, $^2J_{PC}$ = 10.0 Hz, C=O)*, 172.52 (d, $^3J_{PC} = 9.5$ Hz, C=O)*ppm. Minor isomer (*E*) (41.84%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.48$ (3H, t, $^3J_{HH} = 6.9$ Hz, CH_3), 1.25 (3H, t,$^3J_{HH=}$7.4 Hz, CH_3), 5.12 (1H, d, $^3J_{PH}$ =18.0 Hz, P=C-CH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.97$ and 15.02 (2 CH_3), 41.22 (d, $^1J_{PC} = 128.8$ Hz, P=C), 49.04 (d, $^2J_{PC}$ =13.4 Hz, P=C-CH), 57.54 and 58.28 (2 OCH_2), 112.40 (CH), 121.24 (CH), 126.12 (d, $^1J_{PC}$ = 90.9 Hz, C^{ipso}), 128.44 (d,$^3J_{PC} = 12.7$ Hz, CH^{meta}), 132.36 (d, $^4J_{PC} = 2.8$ Hz, CH^{para}), 133.07 (CH), 133.46 (d, $^2J_{PC} = 9.8$ Hz, CH^{ortho}), 148.49 (CH), 160.05 (C) ppm.

Dimethyl 2-[(2-Furylmethyl)sulfanyl)]-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5c)

White powder, 0.93 g, mp 159–161°C yield 90%; IR (KBr) (ν_{max}, cm^1) 1741 and 1641(C=O). Major isomer (*Z*) (53%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.90$ and 3.55 (6H, 2s, 2 CH_3), 3.74–3.83 (2H, m, CH_2)*, 5.88 (1H, d, $^3J_{PH}$ =11.8 Hz, P=C-CH)*, 6.20–7.60 (36H, m, arom)*ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 29.10$ (CH_2), 40.92 (d, $^1J_{PC} = 117.9$ Hz, P=C), 48.33 (d, $^2J_{PC}$ =16.0 Hz, P=C-CH*, 49.04 and 52.34 (2 OCH_3), 106.75 (CH)*, 110.12 (CH)*, 126.31 (d, $^1J_{PC} = 88.0$ Hz, C^{ipso}), 128.62 (d,$^3J_{PC} = 11.2$ Hz, CH^{meta})*, 131.93 (d, $^4J_{PC} = 2.6$ Hz, CH^{para})*, 133.72 (d, $^2J_{PC} = 9.8$ Hz, CH^{ortho})*, 141.52 (CH)*, 152.44 (C)*, 170.31 (d, $^2J_{PC}$ = 13.9 Hz, C=O)*, 173.13 (d, $^3J_{PC} = 9.5$ Hz, C=O)*ppm. Minor isomer (*E*) (47%) ^{1}H NMR (500 MHz, $CDCl_3$):$\delta = 3.37$ and 3.57 (6H, 2s, 2 CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 29.42$ (CH_2), 42.92 (d, $^1J_{PC}$ = 130.6 Hz, P=C), 49.03 and 50.31 (2 OCH_3), 127.02 (d, $^1J_{PC} = 89.7$ Hz, C^{ipso}) ppm.

Diethyl 2-[(2-Furylmethyl)sulfanyl)]-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5d)

White powder, 0.89 g, mp 178–181°C yield 82%; IR (KBr) (ν_{max}, cm^1) 1741 and 1641(C=O). Major isomer (*Z*) (54.75%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.30$ (3H, t, $^3J_{HH} = 7.0$ Hz, CH_3), 1.20 (3H, t,$^3J_{HH=}$7.0 Hz, CH_3), 3.46–3.62 (4H, m, OCH_2)*, 3.72–3.85 (2H, m, CH_2)*, 3.89–4.01 (4H, m, OCH_2)*, 5.87 (1H, d, $^3J_{PH}$ =19.2 Hz, P=C-CH)*, 6.21–7.62 (36H, m, arom)* ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.02 and 14.11 (2 CH_3), 28.92 (CH_2)*, 40.59 (d, $^1J_{PC} = 127.2$ Hz, P=C), 49.95 (d, $^2J_{PC}$ =9.2 Hz, P=C-CH), 60.76 and 61.06 (2 OCH_2), 106.63 (CH), 110.12 (CH), 127.26 (d, $^1J_{PC}$ = 93.2 Hz, C^{ipso}), 128.45 (d,$^3J_{PC}$ = 7.02 Hz, CH^{meta}), 131.80 (d, $^4J_{PC}$ = 2.52 Hz, CH^{para}), 133.78 (d, $^2J_{PC}$ = 9.9 Hz, CH^{ortho}), 141.38 (CH), 152.62 (C), 168.71 (d, $^2J_{PC}$ = 10.0 Hz, C=O)*, 172.51 (d, $^3J_{PC}$ = 9.5 Hz, C=O)*ppm. Minor isomer (*E*) (45.25%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.06$ (3H, t, $^3J_{HH} = 6.9$ Hz, CH_3), 1.22 (3H, t,$^3J_{HH=}$7.0 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ =13.88 and 14.07 (2 CH_3), 42.03 (d, $^1J_{PC}$ = 143.78 Hz, P=C), 48.53 (d, $^2J_{PC}$ =10.1 Hz, P=C-CH), 61.06 and 62.36 (2 OCH_2), 108.33 (CH), 110.50 (CH), 126.56 (d, $^1J_{PC}$ = 84.84 Hz, C^{ipso}), 128.58 (d,$^3J_{PC}$ = 12.7 Hz, CH^{meta}), 131.86 (d, $^4J_{PC}$ = 2.8 Hz, CH^{para}), 133.82 (d, $^2J_{PC}$ = 9.8 Hz, CH^{ortho}), 142.39 (CH), 150.36 (C) ppm.

Dimethyl 2-[(1-Phenyl-1H-1,2,4-triazol-5-yl)sulfanyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5e)

White powder, 1.10 g, mp 110–113°C yield 95%; IR (KBr) (νmax, cm^{-1}): 1741 and 1641 (C=O). Major isomer (*Z*) (56.3%) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.22 and 3.79 (6H, 2s, 2 CH_3), 5.53 (1H, d, $^3J_{PH}$ =15.8 Hz, P=C-CH), 7.42–8.00 (42H, m, arom)*ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 39.75$ (d, $^1J_{PC} = 132.9$ Hz, P=C), 49.44 and 52.98 (2 OCH_3), 63.13 (d, $^2J_{PC}$ =17.7 Hz, P=C-CH), 123.30 (CH)*, 125.44 (d, $^1J_{PC}$ = 80.5 Hz, C^{ipso}), 128.48 (CH), 129.21 (d, $^3J_{PC} = 17.7$ Hz, CH^{meta})*, 131.98 (CH), 132.00 (CH), 132.42 (CH^{para})*, 133.60 (d, $^2J_{PC} = 9.2$ Hz, CH^{ortho})*, 135.17 (C)*, 162.72 (C)*, 169.18 (d, $^2J_{PC}$ = 12.2 Hz, C=O)*, 169.65 (C=O)ppm. Minor Isomer (*E*) (43.7%) ^{1}H NMR (500 MHz, $CDCl_3$):δ = 3.65 and 3.76 (6H, 2s, 2 CH_3), 5.65 (1H, d, $^3J_{PH}$ = 16.4 Hz, P=C-CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 40.70$ (d, $^1J_{PC} = 137.9$ Hz, P=C), 50.56 and 52.84 (2 OCH_3), 62.46 (d, $^2J_{PC}$ =17.0 Hz, P=C-CH), 126.17 (d, $^1J_{PC} = 80.5$ Hz, C^{ipso}), 128.57 (CH), 132.07 (CH), 132.15 (CH), 169.70 (C=O) ppm.

Diethyl 2-[(1-Phenyl-1H-1,2,4-triazol-5-yl)sulfanyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5f)

White powder, 1.20 g, mp 102–104°C yield 98%; IR (KBr) (νmax, cm^{-1}): 1741 and 1641 (C=O). Major isomer (*Z*) (55.3%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.50$ (3H, t, $^3J_{HH} = 7.0$ Hz, CH_3), 1.28 (3H, t,$^3J_{HH=}$7.2 Hz, CH_3), 3.78–4.30 (8H, m, OCH_2)*, 5.53 (1H, d, $^3J_{PH}$ =14.7 Hz, P=C-CH), 7.34–8.00 (42H, m, arom)* ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.13$ and 14.20 (2 CH_3), 58.47 (d, $^1J_{PC} = 98.2$ Hz, P=C)*, 61.83 (2 OCH_2), 63.20 (d, $^2J_{PC}$ =16.7 Hz, P=C-CH)*, 123.37 (CH)*, 126.38 (d, $^1J_{PC}$ = 90.9 Hz, C^{ipso}), 128.48 (CH), 128.99 (d,$^3J_{PC} = 10.9$ Hz, CH^{meta})*, 131.99 (CH), 132.09 (CH), 132.33 (CH^{para})*, 133.65 (d, $^2J_{PC} = 9.2$ Hz, CH^{ortho})*, 135.23 (C)*, 162.83 (C)*, 169.50 (d, $^2J_{PC} = 11.9$ Hz, C=O)*, 169.25 (d, $^2J_{PC} = 6.5$ Hz C=O)*ppm. Minor isomer (*E*) (44.7%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.23$ (3H, t, $^3J_{HH} = 7.2$ Hz, CH_3), 1.33 (3H, t,$^3J_{HH=}$7.0 Hz, CH_3), 5.50 (1H, d, $^3J_{PH}$ =14.05 Hz, P=C-CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.90$ and 14.74 (2 CH_3), 61.28 (2 OCH_2), 125.69 (d, $^1J_{PC}$ = 82.4 Hz, C^{ipso}), 128.58 (CH), 132.0 (CH), 132.17 (CH) ppm.

Dimethyl 2-[(2-Amino-2-thioxoethanthioyl)amino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5g)

Yellow powder, 0.99 g, mp 162–164°C yield 95%; IR (KBr) (νmax, cm^{-1}): 3400, 3227 (NH_2, NH), 1753 and 1636 (C=O), 1519, 1518 (C=S). Major isomer, (E) (54.0%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.60$ and 3.74 (6H, 2s, 2 CH_3), 4.98–5.06 (1H, m, P=C-CH)*, 7.47–7.75 (30H, m, arom)*, 10.93 (2H, brs, NH_2)*, 11.06 (1H, brs, NH)* ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 43.33$ (d, $^1J_{PC} = 135.6$ Hz, P=C), 50.37 and 52.42 (2 OCH_3), 59.89 (d, $^2J_{PC}$ =17.6 Hz, P=C-CH), 126.28 (d, $^1J_{PC} = 91.0$ Hz, C^{ipso}), 128.84 (d,$^3J_{PC} = 12.1$ Hz, CH^{meta})*, 132.16 (CH^{para})*, 133.88 (CH^{ortho})*, 170.04 (d, $^2J_{PC} = 13.3$ Hz, C=O)*, 171.72 (C=O)*, 183.09 and 183.59 (C=S)*ppm. Minor isomer, (Z) (46.0%) ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 3.18 and 3.75 (6H, 2s, 2 CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 42.12 (d, $^1J_{PC} = 123.0$ Hz, P=C), 49.29 and 52.43 (2 OCH_3), 58.92 (d, $^2J_{PC}$ =15.3 Hz, P=C-CH), 125.65 (d, $^1J_{PC} = 92.8$ Hz, C^{ipso}) ppm.

Diethyl 2-[(2-Amino-2-thioxoethanthioyl)amino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5h)

Yellow powder, 0.99 g, mp 170–172°C, yield 90%; IR (KBr) (νmax, cm^{-1}): 3400, 3227 (NH_2, NH), 1753 and 1636 (C=O), 1519 and 1518 (C=S). Major isomer, (E) (61.4%)^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.25$ (9H, t,$^3J_{HH=}$6.7 Hz, 3 CH_3)*, 3.71–4.22 (8H, m, OCH_2)*, 4.98–5.03 (1H, m,

P=C-CH)*, 7.26–7.75 (30H, m, arom)*, 10.97 (2H, brs, NH_2)*, 11.08 (1H, brs, NH)* ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.23$ and 14.96 (2 CH_3), 42.99 (d, $^1J_{PC} = 135.6$ Hz, P=C)*, 58.53 and 61.13 (2 OCH_2), 59.82 (d, $^2J_{PC}$ =16.1 Hz, P=C-CH), 126.55 (d, $^1J_{PC} = 91.4$ Hz, C^{ipso}), 128.72 (d,$^3J_{PC} = 11.9$ Hz, CH^{meta})*, 132.03 (d, $^4J_{PC} = 2.4$ Hz, CH^{para})*, 133.91 (d, $^2J_{PC} = 9.7$ Hz, CH^{ortho})*, 169.83 (d, $^2J_{PC} = 17.1$ Hz, C=O)*, 171.07 (C=O)*, 183.19 and 183.64 (C=S)*ppm. Minor isomer (Z) (38.6%)^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.45$ (3H, t, $^3J_{HH} = 6.1$ Hz, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.91$ and 14.24 (2 CH_3), 41.86 (d, $^1J_{PC}$ = 138.3 Hz, P=C), 57.79 and 61.12 (2 OCH_2), 58.89 (d, $^2J_{PC}$ =16.0 Hz, P=C-CH), 125.92 (d, $^1J_{PC} = 91.6$ Hz, C^{ipso}), 169.64 (d, $^2J_{PC} = 17.4$ Hz, C=O) ppm.

Dimethyl 2-[[Ethylanilino)carbothioyl](1-naphtyl)amino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene) Succinate (5i)

White powder. 0.81 g, mp 153–155°C, yield 76%; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1741 and 1641 (C=O). Major isomer (*Z*) (71%) ^1H NMR (500 MHz, $CDCl_3$): δ = (3H, t,^{3} J_{HH} =7.0 Hz, CH_3), 3.42–3.48 (4H, m, $2CH_2$) *, 2.68 and 4.00 (6H, 2s, 2 OCH_3), 4.04 (1H, d, $^3J_{PH} = 13.8$ Hz, P=C-CH)*, 6.17–7.76 (54 H, m, arm)*.^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 12.84$ (CH_3), 42.66 (d, $^1J_{PC} = 136.0$Hz, P=C), 48.54 (CH_2), 51.48 and 52.21 (2 OCH_3), 68.22 (d, $^2J_{PC} = 19.5$ Hz, P=C-CH) ,124.53–145.94 (carbons of aromatic rings)*, 169.11 (d, $^2J_{PC} = 13.4$ Hz, C=O), 173.92 (d, $^3J_{PC}$ = 14.2 Hz, C=O), 188.81 (C=S). Minor isomer (*E*) (29%), ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.26$ (3H, t, $^3J_{HH} = 7.1$ Hz,CH_3), 3.37 and 3.93 (6H, 2S, 2 OCH_3) . ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 12.89$ (CH_3) , 42.66 (d, $^1J_{PC} = 136.9$ Hz, P=C), 49.60 (CH_2), 51.69 and 52.09 (2 OCH_3), 67.20 (d, $^2J_{PC} = 20.1$ Hz, P=C-CH), 169.97 (d, $^2J_{PC} = 17.7$ Hz, C=O), 173.93(d, $^3J_{PC} = 14.1$ Hz, C=O), 189.13 (C=S).

REFERENCES

[1] P. Laszlo, *Organic Reactions: Simplicity and Logic* (Wiley-VCH, New York, 1995).
[2] D. E. C. Corbridge, *Phosphorus: An Outline of the Chemistry, Biochemistry, and Uses*, 5th ed. (Elsevier, Amsterdam, 1995).
[3] I. Yavari, Z. Hossaini, and E. Karimi, *Monatsh Chem*., **138,** 1267 (2007).
[4] I. Yavari, N. Zabarjad-Shiraz, and H. R. Bijanzadeh, *Phosphorus, Sulfur, and Silicon*, **179,** 1381 (2004).
[5] I. Yavari and E. Karimi, *Phosphorus, Sulfur and Silicon*, **182,** 595 (2007).
[6] M. R. Islami, Z. Hassani, and K. Saidi, *Synthetic Comm*., **33,** 65 (2003).
[7] A. A. Esmaili, M. Ghereghloo, M. R. Islami, and H. R. Bijanzadeh, *Tetrahedron,* **59,** 4785 (2003).

[8] A. Ramazani, A. R. Kazemizadeh, E. Ahmadi, N. Noshiranzadeh, and A. Souldozi, *Current Organic Chemistry*, **11,** 18 (2007).
[9] X. L. Zhao, Y. F. Zhao, S. C. Guo, H. S. Song, D. Wang, and P. Gong, *Molecules*, **12,** 1136 (2007).
[10] Y. Zheng, S. Brown, W. O. Ledig, C. Mussinan, and C. Tang Ho, *J. Agric. Food Chem*., **45,** 894 (1997).
[11] D. S. Mottram and I. C. C. Nobrega, *J. Agric. Food Chem*., **50,** 4080 (2002).
[12] T. Shibamoto and G. F. Russell, *J. Agric. Food. Chem*., **25,** 109 (1977).
[13] R. Kerscher and W. Grosch, *J. Agric. Food. Chem*., **46,** 1954 (1998).
[14] D. S. Mottram and M. S. Madruga, *J. Agric. Food. Chem*., **43,** 189 (1995).
[15] T. S. Lobana, R. Verma, and R. Singh, *Transition Met. Chem*., **23,** 25 (1998).
[16] E. S. C. Raper, *Chem. Rev*., **153,** 199 (1996).
[17] C. Vetter, C. Wagner, J. Schmidt, and D. Steinborn, *Inorganica Chimica Acta*., **359,** 4326 (2006).
[18] M. Friedman and F. F. Bautista, *J. Agric. Food. Chem*., **43,** 69 (1995).
[19] A. Krauze, S. Germane, O. Eberlins, I. Sturms, V. Klusa, and G. Duburs, *Eur. J. Med. Chem*., **34,** 301 (1999).
[20] O. V. Mikhailov, *Transition. Met. Chem*., **25,** 552 (2000).
[21] O. V. Mikhailov and M. A. Kazymova, *Transition Met. Chem*., **23,** 195 (1998).
[22] D. D. Perrin, *Organic Complexing Reagents: Structure, Behavior and Application to Inorganic Analysis* (Interscience Publishers, New York, 1964).
[23] J. Caesar, D. V. Griffiths, P. A. Griffiths, and T. J. Tebby, *Chem. Soc. Perkin Trans*., **1,** 2425 (1989).
[24] J. Caesar, D. V. Griffiths, P. A. Griffiths and T. J. Tebby, *Chem. Soc. Perkin Trans*., **1,** 2329 (1990).
[25] M. R. Islami, F. Mollazehi, A. Badiei, and H. Sheibani, *Arkivoc*., **15,** 25 (2005).
[26] M. R. Islami and M. Yazdi Rouh-Alamini, *Phosphorus, Sulfur, and Silicon*, **182,** 2919 (2007).
[27] V. Nair, C. Rajesh, A. U. Vinod, S. Bindu, A. R. Sreekanth, J. S. Mathess, and L. Balagopal, *Acc. Chem. Res*., **36,** 899 (2003).
[28] L. Van Meervelt, R. N. Vydzhak, V. S. Brovarets, N. I. Mishchenko, and B. S. Drach, *Tetrahedron*, **50,** 1889 (1994).
[29] S. M. Habibi Khorassani, M. T. Maghsoodlou, A. Ebrahimi, H. Roohi, and M. Zakarianezhad, *J. Iran Chem. Soc*., **3,** 223 (2006).
[30] H. J. Bestmann, G. Joachim, T. Lengyel, J. F. Oth, R. Merenyi, and H. Weitkamp, *Tetrahedron Lett*., 3355 (1966).
[31] H. J. Bestmann and J. P. Snyder, *J. Am. Chem. Soc.*, **89,** 3963 (1967).
[32] D. L. Hooper and S. Garagan, *J. Org. Chem.*, **59,** 1126 (1994).