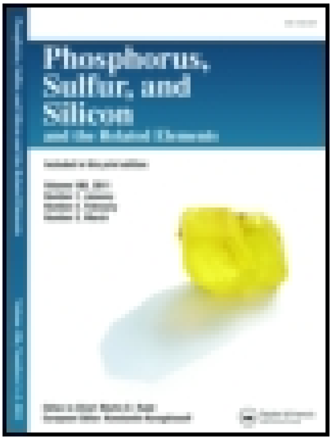

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A Simple and an Efficient Method for Preparation of New Phosphorus Ylides Containing Several Functional Groups Using Aryl Thiourea

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A Simple and an Efficient Method for Preparation of New Phosphorus Ylides Containing Several Functional Groups Using Aryl Thiourea

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New phosphorus ylides were prepared in a convenient way using the addition of $Pb(OAc)_2$ *to aryl thiourea followed by condensation of the resulted compounds with acetylenic esters in the presence of triphenylphosphine.*

Keywords Acetylenic compounds; phosphorus ylides; thiourea

INTRODUCTION

The synthesis and chemistry of phosphorus ylides have been attracted considerable attention due to their applications in the preparation of organic compounds.[1–4] Also, these compounds are an interesting class of materials that have been used as building blocks in the synthesis of heterocyclic systems such as pyrazoloisoindole, pyrrolizine and pyrroloisoindole derivatives.[5–7] Some stable phosphorus ylides were used as precursors in the preparation of drugs.[8] On the other hand, most of the phosphorus ylides are unstable systems and they are known to react easily with other compounds such as, halogens,[9,10] peroxyacids,[11] and carbonyl compounds.[12–15]

In recent years, the synthesis of succinic esters connected to phosphorus atom has drawn much more attention.[16–22] Since the synthetic application of these compounds has increased enormously in organic synthesis, we now wish to report a method for the synthesis of new phosphorus ylides containing several functional groups by reaction of

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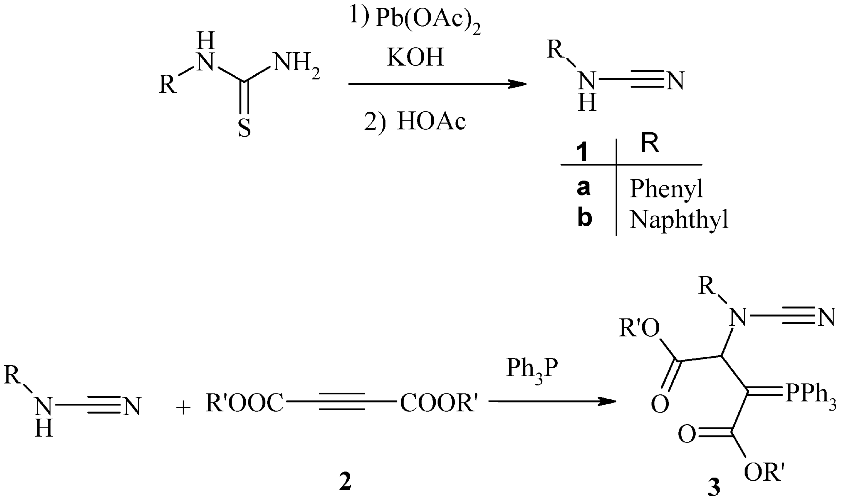
$Pb(OAc)_2$ with aryl thiourea and then condensation of the resulted compounds with acetyletic esters in the presence of triphenylphosphine as a good nucleophile.

RESULTS AND DISCUSSION

At first, N-aryl cyanamides were obtained from the reaction between N-phenyl or N-naphthyl urea and $Pb(OAc)_2$ in the presence of potassium hydroxide solution as a base under reflux[23] (Scheme 1).

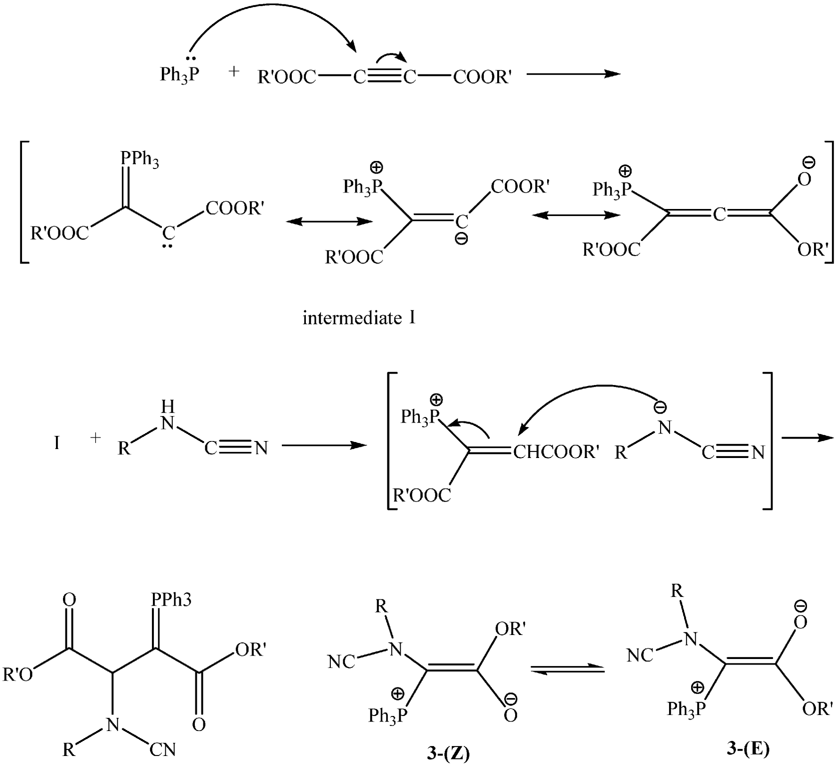


1	R
a	Phenyl
b	Naphthyl

3	R	R'
a	phenyl	Me
b	naphthyl	Me
c	naphthyl	Et

SCHEME 1

The results presented here are based on the proposed sequence below (Scheme 2). It is known that the reaction of acetylenic esters and Ph_3P produces the carbene-ylide intermediate **I** which is sufficiently stabilized by resonance.[24,25] Thus, compounds **3a–c** are apparently obtained from the initial addition of triphenylphosphine as a good nucleophile to acetylenic esters as a Michael acceptor[26] and concomitant protonation of the carbene-ylide intermediate **I** by the NH-acid. Then positively charged ion is attacked by the nitrogen of the conjugated base of the



3a-c

SCHEME 2

NH-acid to form stable phosphorus ylides containing several functional groups **3**.

The product structures **3a–c** were identified by IR, ^{1}H, and ^{13}C NMR spectra. The ^{1}H NMR and ^{13}C NMR spectral data of new ylides **3a–c** exhibited a mixture of two conformational isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in 3-**(E)**, 3-**(Z)** geometrical isomer 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.[27–29]

Insertion of nitrogen in the chain was characterized by disappearance of band at near 3300 cm^{-1} of N—H and appearance of new peaks near 1740 and 1645 cm^{-1} for C=O stretching. The ^{1}H NMR spectra of **3a** showed four sharp signals due to methoxy protons of ester groups at $\delta = 3.18$, 3.62, 3.72, and 3.75 ppm. Methine protons appeared as two doublet peaks at $\delta = 4.12$ and 4.14 ppm for the Z and E geometrical isomers. The aromatic protons appeared as a multiplet at $\delta = 6.56$–7.44 ppm. The ^{13}C NMR spectrum of **3a** 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 **3a**, it helps in assignment of signals by long range spin-spin couplings with ^{1}H and ^{13}C nuclei.

The ^{1}H and ^{13}C NMR spectra of compound **3b** are similar to those of **3a**, except for the signals from the aromatic ring of naphthaline, which appear as characteristic resonance lines with the corresponding chemical shifts. The ^{1}H and ^{13}C NMR spectroscopic data for compounds **3c** are also consistent with the proposed structures.

In conclusion, we have presented an efficient synthetic method for formation of new stable phosphorus ylides. The simplicity of experimental procedure and availability of the starting materials thus render this method, an experimental attractive approach for the synthesis of these compounds.

EXPERIMENTAL

All common reagents and solvents were used as obtained from commercial suppliers without further purification. The ^{1}H, and ^{13}C NMR spectra were recorded on a Bruker BRUKER DRX-500 AVANCE (^{1}H at 500 MHz, and ^{13}C at 125.77 MHz,). Melting points were obtained on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses for C, H and N for compound **3c** as an example were performed by University of Tarbiat Moalem using a Heracus CHN-O-Rapid analyzer. IR spectra were measured on a Mattson 1000 FT-IR spectrometer. Phenyl cyanamide **1a** and Naphthyl cyanamide **1b** were obtained as described in the literature.[23]

Dimethyl 2-(cyanoanilino)-3-(1,1,1-triphenyl-λ^5 phosphanylidene) Succinate (3a)

At ambient temperature (0.24 ml, 2 mmol) of dimethyl acetylenedicarboxylate was added dropwise to a stirred solution of (0.53 g, 2 mmol) of triphenylphosphine and (0.24 g, 2 mmol) of phenyl cyanamide in a 10 mL ethyl acetate. After the addition was complete (approximately 60 minutes), the mixture was stirred for another 10 h and filtered. The solid collected in the filter was washed thoroughly with ethyl acetate to give a white powder. (0.81 g, m.p. 132–134°C, yield 76%); IR (KBr) ($\nu_{\max,}$ cm^{-1}): 2237 (CN), 1741 and 1666 (C=O). Isomer (E) (57%) ^{1}H

NMR: δ 3.62, 3.72 (6H, 2s, 2 OCH_3), 4.14 (1H, d, $^3J_{PH}$18.2 Hz, P=C—CH), 6.56–7.44 (40 H, m, arm).[30,] ^{13}C NMR: δ 42.45 (d, $^1J_{PC}$137.4 Hz, P=C), 50.44, 52.60 (2 OCH_3), 62.05 (d, $^2J_{PC}$ 15.6 Hz, P=C—CH) ,115.49 (C—N), 116.04–133.75 (carbons of aromatic rings),[15–18,30] 170.19 (d, $^2J_{PC}$17.7 Hz, C=O), 171.13 (d, $^3J_{PC}$ 13.9 Hz, C=O). Isomer (Z) (43%), ^{1}H NMR: δ 3.18, 3.75 (6H, 2s, 2 OCH_3), 4.13 (1H, d, $^3J_{PH}$13.9 Hz, P=C—CH). ^{13}C NMR: δ 40.73 (d, $^1J_{PC}$127.7 Hz, P=C), 49.44 and 52.79 (2OCH_3), 63.08 (d, $^2J_{PC}$16.2Hz, P=C-CH), 112.93 (C—N), 169.05 (d, $^2J_{PC}$12.7 Hz, C=O), 171.24(d, $^3J_{PC}$13.8 Hz, C=O).

Dimethyl 2-[cyano(1-naphthyl)amino]-3-(1,1,1-triphenyl-λ^5phosphanylidene) Succinate (3b)

(0.88 g, m.p. 168–170°C, yield 76%); IR (KBr) ($\nu_{max,}$ cm^{-1}): 2212 (CN),1765 and 1619 (C=O). Isomer (Z) (57 %) ^{1}H NMR: δ 3.00, 3.54 (6H, 2s, 2 OCH_3), 4.58 (1H, d, $^3J_{PH}$19.6 Hz, P=C—CH), 7.04-7.99 (44 H, m, arm) .[30,] ^{13}C NMR: δ 41.40 (d, $^1J_{PC}$125.6 Hz, P=C), 45.86 (d, $^2J_{PC}$12.8 Hz, P=C—CH), 48.71, 51.70 (2 OCH_3), 112.50 (C—N),121.44–133.72(carbons of aromatic rings),[30] 169.02 (d, $^2J_{PC}$13.1 Hz, C=O), 170.20 (d, $^3J_{PC}$18.1 Hz, C=O). Isomer (E) (43%), ^{1}H NMR: δ 3.643, 3.55 (6H, 2s, 2 OCH_3), 4.42 (1H, d, $^3J_{PH}$20.0 Hz, P=C—CH). ^{13}C NMR: δ 41.73 (d, $^1J_{PC}$134.04 Hz, P=C), 45.19 (d, $^2J_{PC}$13.6Hz, P=C—CH), 49.71 and 51.90 (2 OCH_3),111.00 (C—N), 174.25 (d, $^2J_{PC}$7.4Hz, C=O), 174.65(d, $^3J_{PC}$8.0Hz, C=O).

Diethyl 2-[cyano(1-naphthyl)amino]-3-(1,1,1-triphenyl-λ^5phosphanylidene) Succinate (3c)

(0.92 g, m.p. 170–172°C, yield 75%); IR (KBr) (ν_{max}, cm^{-1}): 2237 (CN), 1716,1641 (C=O). Anal. Calcd. for $C_{37}H_{33}N_2O_4P$ (600.64): C,73.99; H, 5.54;N, 4.66%. Found: C,73.54; H, 5.66;N, 4.65%. Isomer (Z) (63%), ^{1}H NMR: δ 0. 37 (3H, t, $^3J_{HH}$6.9 Hz, CH_3), 1.17 (3H, t,$^3J_{HH}$7.1 Hz, CH_3), 3.53–4.09 (8 H, m, 4 OCH_2),[30] 4.56 (1H, d, $^3J_{PH}$20.0 Hz, P=C—CH), 7.02–7.99 (44H, m, arm).[30,] ^{13}C NMR: 13.88 and 14.16 (2 CH3), 41.17 (d, ,$^1J_{PC}$ 124.9Hz, P=C), 45.08(d, $^2J_{PC}$ 12.2 Hz P=C—CH), 56.89 and 60.03 (2 OCH_2), 113.04 (C—N), 121.39–133.24 (carbons of aromatic rings),[30] 168.57 (d, $^2J_{PC}$ 12.9 Hz, C=O), 173.84 (d, $^2J_{PC}$ 7.7 Hz, C=O). Isomer (E) (37%), ^{1}H NMR: δ 1.04(3H, t, $^3J_{HH}$6.8 Hz, CH_3), 1.19 (3H, t, $^3J_{HH}$ 6.5 Hz, CH_3), 4.34 (1H, d, $^3J_{PH}$20.2 Hz, P=C—CH) .^{13}C NMR: 14.11 and 14.90 (CH_3), 41.58 (d, ,$^1J_{PC}$ 132.7 Hz, P=C), 45.08 (d,$^2J_{PC}$ 12.2 Hz, P=C—H), 57.32 and 60.11 (2 OCH_2), 111.12 (C—N),169.88 (d, $^2J_{PC}$ 19.1 Hz, C=O), 173.67 (d, $^2J_{PC}$ 9.5Hz, C=O).

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