
**Journal of Sulfur Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

# Three-component reaction between triphenylphosphine, dialkyl acetylenedicarboxylate and 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thiones: an efficient one-pot synthesis of stable phosphorus ylides

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Online publication date: 07 April 2010

**To cite this Article** Mosslemin, Mohammad Hossein , Anary-Abbasinejad, Mohammad , Hassanabadi, Alireza and Bagheri, Mohammad Ali(2010) 'Three-component reaction between triphenylphosphine, dialkyl acetylenedicarboxylate and 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thiones: an efficient one-pot synthesis of stable phosphorus ylides', Journal of Sulfur Chemistry, 31: 2, 135 — 139
**To link to this Article: DOI:** 10.1080/17415991003682617
**URL:** http://dx.doi.org/10.1080/17415991003682617

*Journal of Sulfur Chemistry*
Vol. 31, No. 2, April 2010, 135–139

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# Three-component reaction between triphenylphosphine, dialkyl acetylenedicarboxylate and 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thiones: an efficient one-pot synthesis of stable phosphorus ylides

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(*Received 8 January 2010; final version received 7 February 2010*)

Protonation of the reactive 1:1 intermediate produced in the reaction between dialkyl acetylenedicarboxylates and triphenylphosphine by 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thione leads to vinylphosphonium salts which undergo Michael addition with the conjugate base of the NH-acid to produce highly functionalized, salt-free phosphorus ylides in excellent yields.

**Keywords:** addition reaction; dialkyl acetylenedicarboxylates; phosphorus ylides; triphenylphosphine; NH-acid

## 1. Introduction

Organophosphorus compounds, those bearing a carbon atom bound directly to a phosphorus atom, are synthetic targets of interest, at least because of their value for a variety of industrial, biological, and chemical synthetic uses (*1–3*). Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of an appropriate phosphonium salt with a base; the corresponding phosphonium salts are usually obtained from the phosphine and an alkyl halide (*1, 2*). Phosphonium salts are also prepared by the Michael addition of phosphorus nucleophiles to activated olefins (*1, 2)*. Reaction of acetylenic esters with triphenylphosphine in the presence of an organic compound possessing an acidic hydrogen has been recently reported to produce phosphorus ylides (*4–12*). In continuation of our works on the reaction between triphenylphosphine and acetylene diesters in the presence of organic N–H, O–H or C–H acids (*13a–f*), we herein report an efficient synthetic route to stable phosphorus ylides using three-component reaction between dialkyl acetylenedicarboxylates (DAADs), triphenylphosphine and 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thione (**2**).

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ISSN 1741-5993 print/ISSN 1741-6000 online

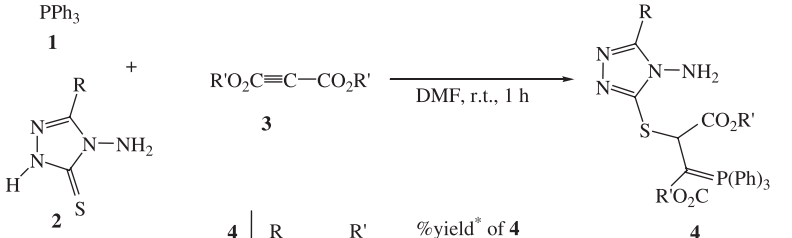
DOI: 10.1080/17415991003682617
http://www.informaworld.com

## 2. Results and discussion

The reaction of the 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thione (**2**) with DAAD (**3**) in the presence of triphenylphosphine 1 leads to the corresponding ylide **4** in good yields (Scheme 1). The $^1$H NMR spectrum of compound **4a** displays two sharp singlets ($\delta$3.13, 3.71 ppm) for the protons of two methoxy groups, a doubled signal for the methine proton at 5.43 ppm ($^3J_{HP} = 16$ Hz) and multiplets between 7.26 and 7.72 ppm for aromatic protons. A broad singlet was observed at 1.69 ppm that disappeared after the addition of a few drops of $D_2O$ to $CDCl_3$ solution of compound **4a**. This signal is related to $NH_2$ protons. The $^{13}$C NMR spectrum of compound **4a** showed 13 distinct signals, which is consistent with the proposed structure. The $^{31}$P NMR spectrum of compound **4a** consists of one signal at 23.2 ppm. This shift is similar to those observed for other stable phosphorus ylides (*14, 15*). The structural assignments made on the basis of the NMR spectra of compounds **4a**–**f** are supported by their IR spectra. The carbonyl region of the spectrum exhibits absorption bands at 1750 cm$^{-1}$ for the ester groups and at 3300 and 3460 cm$^{-1}$ for the $NH_2$ group.

It is reasonable to assume that ylide **4** results from the initial addition of triphenylphosphine to DAAD and subsequent protonation of the 1:1 adduct by the NH-acidic triazole. The positively charged ion **5** is then attacked by the triazole anion **6** to form **4** (Scheme 2).

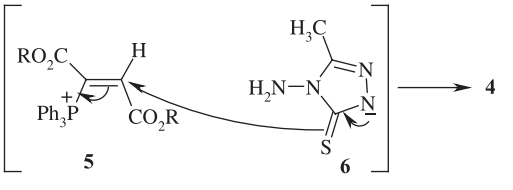
In summary, we report herein that the three-component reaction between DAADs and triphenylphosphine by 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thiones produces functionalized phosphorus ylides in good yields. The advantages of the reported method are simple available




| 4 | R | R' | %yield* of 4 |
|---|---|---|---|
| **a** | Me | Methyl | 93 |
| **b** | Me | Ethyl | 92 |
| **c** | Me | *t*-Butyl | 97 |
| **d** | Et | Methyl | 95 |
| **e** | Et | Ethyl | 93 |
| **f** | Et | *t*-Butyl | 95 |

* Isolated yields

Scheme 1. Three-component reaction between triphenylphosphine, DAADs and 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thiones.




Scheme 2. Suggested mechanism for formation of ylides **4**.

starting materials, short reaction time, simple work-up, neutral reaction conditions and high yields.

## 3. Experimental

All melting points are uncorrected. Elemental analyses were performed at the Analytical Laboratory of Islamic Azad University, Yazd Branch, using a Costech ECS 4010 CHNS-O analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. $^{1}$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer at 500, 128.5 and 202.5 MHz, respectively. $^{1}$H, $^{13}$C and $^{31}$P NMR spectra were obtained on a solution in $CDCl_3$ using TMS as the internal standard or 85% $H_3PO_4$ as the external standard. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

### 3.1. *General procedure*

A magnetically stirred solution of triphenylphosphine (2 mmol) and 4-amino-5-alkyl-2,4-dihydro-1,2,4-triazole-3-thione (2 mmol) in DMF (10 mL) was added dropwise to a mixture of DAAD (2 mmol) in DMF (3 mL) at room temperature for 2 min. The reaction mixture was then stirred for 1 h. Water (50 mL) was added and the solid was filtered off and washed with diethyl ether to give the pure product.



### 3.2. *Dimethyl 2-(4-amino-5-methyl-4H-1,2,4-triazol-3-yl-sulfanyl)-3-(triphenyl-λ$^5$-phosphanylidene)-succinate (4a)*

White powder; yield: 93%; m.p. 160–162°C. IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1750 (C=O), 3300, 3460 ($NH_2$). Analyses: Calcd. for $C_{27}H_{27}N_4O_4PS$: C, 60.66; H, 5.09; N, 10.48. Found: C, 60.4; H, 5.2; N, 10.6. MS (*m*/*z*, %): 534 ($M^+$, 7).

$^{1}$H NMR (500.1 MHz, $CDCl_3$): $\delta$1.69 (2H, s, $NH_2$), 2.40 (3H, s, $CH_3$), 3.13 (3H, s, $OCH_3$), 3.71 (3H, s, $OCH_3$), 5.43 (1H, d, $^{3}J_{PH} = 16$ Hz), 7.26–7.72 (15H, m, aromatic). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$9.8 ($CH_3$), 48.3 ($OCH_3$), 50.5 (d, $^{1}J_{PC} = 126$ Hz,C=P), 51.7 ($OCH_3$), 61.5 (d, $^{2}J_{PC} = 16$ Hz, CH), 125.3 (d, $^{1}J_{PC} = 94$ Hz), 127.8 ($^{2}J_{PC} = 12$ Hz), 132.1 (d, $^{4}J_{PC} = 2$ Hz), 132.8 (d, $^{3}J_{PC} = 10$ Hz), 146.9 (SC=N), 164.6 (NC=N), 169.5 (d, $^{2}J_{PC} = 12$ Hz C=O), 171.3 (d, $^{3}J_{PC} = 17$ Hz C=O). $^{31}$P NMR (202.5 MHz, $CDCl_3$): $\delta$22.82.

### 3.3. *Diethyl 2-(4-amino-5-methyl-4H-1,2,4-triazol-3-yl-sulfanyl)-3-(triphenyl-λ$^5$-phosphanylidene)-succinate (4b)*

White powder; yield: 92%; m.p. 152–154°C. IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1748 (C=O), 3295, 3485 ($NH_2$). Analyses: Calcd. for $C_{29}H_{31}N_4O_4PS$: C, 61.91; H, 5.55; N, 9.96. Found: C, 61.7; H, 5.4; N, 10.2. MS (*m*/*z*, %): 562 ($M^+$, 6).

$^{1}$H NMR (500.1 MHz, $CDCl_3$): $\delta$0.43 (3H, t, $^{3}J_{HH} = 7$ Hz, $CH_3$), 1.15 (3H, t, $^{3}J_{HH} = 7$ Hz, $CH_3$), 1.70 (2H, s, $NH_2$), 1.94 (3H, s, $CH_3$), 3.65 (2H, d, $^{3}J_{HH} = 7$ Hz, $OCH_2$), 3.77 (2H, d, $^{3}J_{HH} = 7$ Hz, $OCH_2$), 5.44 (1H, d, $^{3}J_{PH} = 16$ Hz), 7.26–7.73 (15H, m, aromatic). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$11.3 ($CH_3$), 13.9 and 14.2 ($2CH_3$), 41.3 (d, $^{1}J_{PC} = 122$ Hz, C=P), 57.9 (d, $^{2}J_{PC} = 15$ Hz, CH), 61.7 and 62.6 (2 $OCH_2$), 126.1 (d, $^{1}J_{PC} = 91$ Hz), 128.8 ($^{2}J_{PC} = 12$ Hz), 132.1 (d, $^{4}J_{PC} = 2$ Hz), 133.7 (d, $^{3}J_{PC} = 10$ Hz), 147.3 (SC=N), 165.4 (NC=N), 169.8 (d, $^{2}J_{PC} = 12$ Hz C=O), 170.9 (d, $^{3}J_{PC} = 18$ Hz C=O). $^{31}$P NMR (202.5 MHz, $CDCl_3$): $\delta$22.97.

### 3.4. *Di-t-butyl 2-(4-amino-5-methyl-4H-1,2,4-triazol-3-yl-sulfanyl)-3-(triphenyl-λ$^5$-phosphanylidene)-succinate (4c)*

White powder; yield: 97%; m.p. 165–167°C. IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1744 (C=O), 3395, 3525 ($NH_2$). Analyses: Calcd. for $C_{33}H_{39}N_4O_4PS$: C, 64.06; H, 6.35; N, 9.06. Found: C, 63.9; H, 6.5; N, 9.2. MS (*m*/*z*, %): 618 (M$^+$, 9).

$^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$0.83 (9H, s, *t*-Bu), 1.42 (9H, s, *t*-Bu), 1.45 (2H, s, $NH_2$), 2.32 (3H, s, $CH_3$), 5.43 (1H, d, $^3J_{PH} = 16$ Hz), 7.28-7.97 (15H, m, aromatic). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$11.3($CH_3$), 28.7 and 28.9 (6 $CH_3$ of 2 *t*-Bu), 55.0 (d, $^1J_{PC} = 126$ Hz, C=P), 63.4 (d, $^2J_{PC} = 16$ Hz, CH), 76.7 and 80.5 (2 O-C($CH_3$)$_3$), 127.9 (d, $^1J_{PC} = 94$ Hz), 129.5 ($^2J_{PC} = 12$ Hz), 132.9 (d, $^4J_{PC} = 2$ Hz), 134.1 (d, $^3J_{PC} = 10$ Hz), 147.2 (SC=N), 163.2 (NC=N), 169.5 (d, $^2J_{PC} = 12$ Hz C=O), 171.3 (d, $^3J_{PC} = 17$ Hz C=O). $^{31}$P NMR (202.5 MHz, $CDCl_3$): $\delta$22.78.

### 3.5. *Dimethyl 2-(4-amino-5-ethyl-4H-1,2,4-triazol-3-yl-sulfanyl)-3-(triphenyl-λ$^5$-phosphanylidene)-succinate (4d)*

White powder; yield: 95%; m.p. 124–126°C. IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1751 (C=O), 3265, 3540 ($NH_2$). Analyses: Calcd. for $C_{28}H_{29}N_4O_4PS$: C, 61.30; H, 5.33; N, 10.21. Found: C, 61.5; H, 5.1; N, 10.4. MS (*m*/*z*, %): 548 (M$^+$, 4).

$^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 1.31 (3H, t, $^3J_{HH} = 7 H_Z$, $CH_3$), 1.62 (2H, s, $NH_2$), 2.78 (2H, q, $^3J_{HH} = 7$ Hz, $CH_2$), 3.13 (3H, s, $OCH_3$), 3.72 (3H, s, $OCH_3$), 5.56 (1H, d, $^3J_{PH} = 16$ Hz,), 7.34–7.72 (15H, m, aromatic). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$10.6 ($CH_3$), 18.5 ($CH_2$), 49.8 (d, $^1J_{PC} = 126$ Hz, C=P), 52.4 ($OCH_3$), 52.6 ($OCH_3$), 62.7 (d, $^2J_{PC} = 16$ Hz, CH), 125.9 (d, $^1J_{PC} = 94$ Hz), 128.6 ($^2J_{PC} = 12$ Hz), 132.0 (d, $^4J_{PC} = 2$ Hz), 133.7 (d, $^3J_{PC} = 10$ Hz), 151.3 (SC=N), 165.9 (NC=N), 169.8 (d, $^2J_{PC} = 12$ Hz C=O), 170.1 (d, $^3J_{PC} = 17$ Hz, C=O). $^{31}$P NMR (202.5 MHz, $CDCl_3$): $\delta$22.75.

### 3.6. *Diethyl 2-(4-amino-5-ethyl-4H-1,2,4-triazol-3-yl-sulfanyl)-3-(triphenyl-λ$^5$-phosphanylidene)-succinate (4e)*

White powder; yield: 93%; m.p. 113–115°C. IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1749 (C=O), 3280, 3535 ($NH_2$). Analyses: Calcd. for $C_{30}H_{33}N_4O_4PS$: C, 62.49; H, 5.77; N, 9.72. Found: C, 62.6; H, 5.6; N, 9.9. MS (*m*/*z*, %): 576 (M$^+$, 7).

$^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$0.45 (3H, t, $^3J_{HH} = 7$ Hz, $CH_3$), 1.16 (3H, t, $^3J_{HH} = 7$ Hz, $CH_3$), 1.32 (3H, s, $CH_3$), 1.73 (2H, s, $NH_2$), 2.77 (2H, d, $^3J_{HH} = 7$ Hz, $CH_2$), 3.78 (2H, d, $^3J_{HH} = 7$ Hz, $OCH_2$), 4.08 (2H, d, $^3J_{HH} = 7$ Hz, $OCH_2$), 5.62 (1H, d, $^3J_{PH} = 16$ Hz,CH), 7.31–7.62 (15H, m, aromatic). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$10.5 ($CH_3$), 13.9 and 14.2 (2 $CH_3$), 18.5 ($CH_2$), 39.3 (d, $^1J_{PC} = 122$ Hz, C=P), 57.8 (d, $^2J_{PC} = 15$ Hz, CH), 61.4 and 62.9 (2 $OCH_2$), 126.5 (d, $^1J_{PC} = 91$ Hz), 128.7 (d, $^2J_{PC} = 12$ Hz), 132.0 (d, $^4J_{PC} = 2$ Hz), 133.8 (d, $^3J_{PC} = 10$ Hz), 151.3 (SC=N), 165.9 (NC=N), 169.7 (d, $^2J_{PC} = 12$ Hz, C=O), 171.0 (d, $^3J_{PC} = 18$ Hz, C=O). $^{31}$P NMR (202.5 MHz, $CDCl_3$): $\delta$22.81.

### 3.7. *Di-t-butyl 2-(4-amino-5-ethyl-4H-1,2,4-triazol-3-yl-sulfanyl)-3-(triphenyl-λ$^5$-phosphanylidene)-succinate (4f)*

White powder; yield: 95%; m.p. 165–167°C. IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1746 (C=O), 3390, 3517 ($NH_2$). Analyses: Calcd. for $C_{34}H_{41}N_4O_4PS$: C, 64.54; H, 6.53; N, 8.85. Found: C, 64.7; H, 6.7; N, 8.9.MS (*m*/*z*, %): 632 (M$^+$, 6).

$^{1}$H NMR (500.1 MHz, $CDCl_3$): $\delta$0.81 (9H, s, *t*-Bu), 1.29 (3H, t, $^{3}J_{HH} = 7$ Hz, $CH_3$), 1.40 (9H, s, *t*-Bu), 1.52 (2H, s, $NH_2$), 2.73 (2H, q, $^{3}J_{HH} = 7$ Hz, $CH_2$), 5.49 (1H, d, $^{3}J_{PH} = 16$ Hz), 7.32–7.91 (15H, m, aromatic). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$10.3 ($CH_3$), 18.6 ($CH_2$), 28.2 and 28.7 (6 $CH_3$ of 2 *t*-Bu), 55.2 (d, $^{1}J_{PC} = 126$ Hz, C=P), 62.8 (d, $^{2}J_{PC} = 16$ Hz, CH), 76.4 and 80.7 (2 O–C$(CH_3)_3$), 127.3 (d, $^{1}J_{PC} = 94$ Hz), 129.4 ($^{2}J_{PC} = 12$ Hz), 132.7 (d, $^{4}J_{PC} = 2$ Hz), 133.8 (d, $^{3}J_{PC} = 10$ Hz), 147.0 (SC=N), 162.9 (NC=N), 169.7 (d, $^{2}J_{PC} = 12$ Hz, C=O), 171.1 (d, $^{3}J_{PC} = 17$ Hz, C=O). $^{31}$P NMR (202.5 MHz, $CDCl_3$): $\delta$ 22.65.

## Acknowledgements

We gratefully acknowledge the financial support from the Research Council of Islamic Azad University of Yazd and The Islamic Azad University of Zahedan of Iran.

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