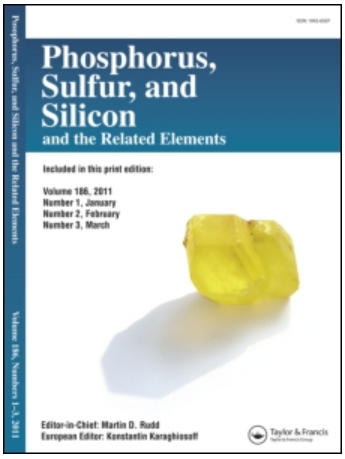


**Phosphorus, Sulfur, and Silicon and the Related Elements**
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http://www.informaworld.com/smpp/title~content=t713618290

# Synthesis of Stable Phosphorus Ylides by the Reaction of $Ph_3P$ With Activated Acetylenes in the Presence of Dimethyl Methoxymalonate

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**To cite this Article** Yavari, Issa and Karimi, Elham(2007) 'Synthesis of Stable Phosphorus Ylides by the Reaction of $Ph_3P$ With Activated Acetylenes in the Presence of Dimethyl Methoxymalonate', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 3, 595 — 600
**To link to this Article: DOI:** 10.1080/10426500601015716
**URL:** http://dx.doi.org/10.1080/10426500601015716

*Phosphorus, Sulfur, and Silicon*, 182:595–600, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601015716

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# Synthesis of Stable Phosphorus Ylides by the Reaction of $Ph_3P$ With Activated Acetylenes in the Presence of Dimethyl Methoxymalonate

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*Triphenylphosphine reacts with dimethyl methoxymalonate in the presence of alkyl propiolates or dialkyl acetylenedicarboxylates to produce trialkyl 3-(1,1,1-triphenyl-$\lambda^5$-phosphanylidene)-1-propene-1,1,2-tricarboxylates or tetraalkyl 3-(1,1,1-triphenyl-$\lambda^5$-phosphanylidene)-1-propene-1,1,2,3-tetracarboxylates in good yields.*

**Keywords** Activated acetylene; phosphorus ylide; triphenylphosphine



## INTRODUCTION

In recent years there has been increasing interest in the synthesis of organophosphorus compounds having a carbon atom bonded directly to the phosphorus atom.[1–3] This interest has resulted from the recognition of the value of such compounds in a variety of biological, industrial, and chemical synthetic uses. A large number of methods have appeared describing novel syntheses of organophosphorus compounds.

The successful nucleophilic attack of trivalent phosphines on a carbon atom is facilitated when the latter is conjugated with a carbonyl group or when it is part of an unsaturated bond system otherwise activated.[1–8] There are many studies on reactions between trivalent phosphorus nucleophiles and $\alpha,\beta$-unsaturated carbonyl compounds in the presence of a proton source such as an alcohol or CH-acid.[8–10] Here we report on a simple one-pot synthesis of stable phosphorus ylides **3** through the reaction of triphenylphosphine ($Ph_3P$) with acetylenic esters **1** in the presence of dimethyl methoxymalonate **2**. This reaction provides an effective route to $\alpha,\beta$-unsaturated ylides **3**.

Received May 30, 2006; accepted August 16, 2006.
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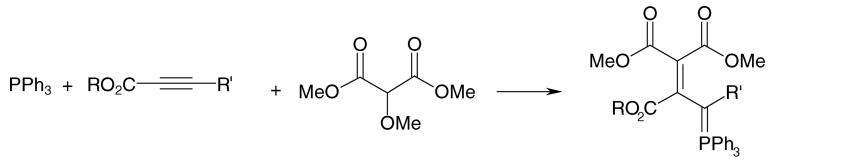
## RESULTS AND DISCUSSION

The reaction between $Ph_3P$ and dimethyl methoxymalonate in the presence of alkyl propiolates or dialkyl acetylenedicarboxylates led to trialkyl 3-(1,1,1-triphenyl-$\lambda^5$-phosphanylidene)-1-propene-1,1,2-tricarboxylates or tetraalkyl 3-(1,1,1-triphenyl-$\lambda^5$-phosphanylidene)-1-propene-1,1,2,3-tetracarboxylates in good yields (Scheme 1).

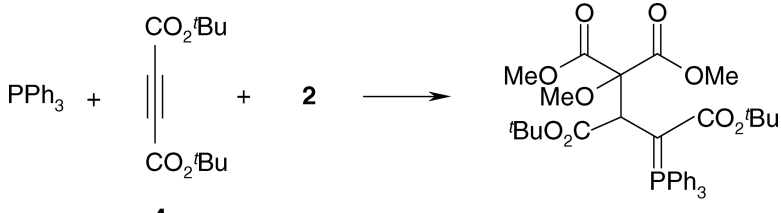



**1** **2**

| 1, 3 | R | R' | Yield of **3** (%) |
|---|---|---|---|
| **a** | Me | H | 82 |
| **b** | Me | H | 85 |
| **c** | Me | $CO_2Me$ | 90 |
| **d** | Et | $CO_2Et$ | 81 |

**SCHEME 1**

Under similar conditions, di-*tert*-butyl acetylenedicarboxylate afforded ylide **5**, which was recovered unchanged after refluxing for 5 h in toluene (Scheme 2).

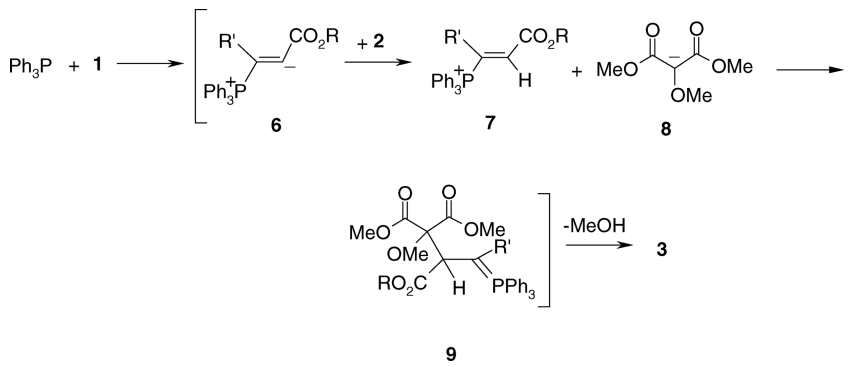



**4** **5**

**SCHEME 2**

On the basis of well-established chemistry of trivalent phosphorus nucleophiles[1–3] it is reasonable to assume that compounds **3** result from the initial addition of $Ph_3P$ to the acetylenic ester and subsequent protonation of the 1:1 adduct **6** by **2** to form **7**. Then the positively charged ion is attacked by the enolate anion of CH-acid to form **9**, which is then converted to the ylide **3** by elimination of MeOH (Scheme 3).

Structures of compounds **3** and **5** were deduced from their elemental analyses and their $^1H$ and $^{13}C$ NMR spectra. The $^1H$ NMR spectrum of **3a** exhibited two singlets at $\delta$ 2.74 and 3.59 ppm, in a 1:2 ratio, for methoxy protons. The CH group appeared as a doublet at $\delta$ 6.44 ppm with $^2J_{PH} = 20.0$ Hz. For the aromatic protons, signals at $\delta$ 7.44–7.61




**SCHEME 3**



ppm were observed. The $^{1}H$ decoupled $^{13}C$ NMR spectrum of **3a** showed 11 signals in agreement with the proposed structure. $^{1}H$ and $^{13}C$ NMR spectra of **3b–3d** were similar to those of **3a** except for the ester moiety, which exhibited characteristic signals with appropriate chemical shifts.

In summary, we have prepared novel ester-containing phosphorus ylides via a one-pot reaction between $Ph_3P$ and acetylenic esters in the presence of dimethyl methoxymalonate. The present method carries the advantage that not only is the reaction performed under neutral conditions, but the substances can be mixed without any activation or modification. Phosphorus ylides **3** and **5** may be considered potentially useful synthetic intermediates.

## EXPERIMENTAL

Dialkyl acetylenedicaboxylates, alkyl propiolates, $Ph_3P$, and compound **2** were obtained from Fluka (Buchs, Switzerland) and were used without further purification. M.p.: Electrothermal-9100 apparatus; uncorrected. IR Spectra: Shimadzu IR-460 spectrometer.$^{1}H$ and $^{13}C$ NMR spectra: Bruker DRX-500 AVANCE instrument in $CDCl_3$ at 500.1 and 125.7 MHz, respectively; $\delta$ in ppm, $J$ in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer in m/z. Elemental analyses (C, H, and N) were performed with a Heraeus CHN-O-Rapid analyzer.

### General Procedure for the Preparation of Compounds 3

To a stirred solution of **2** (0.26 mL, 2 mmol) and acetylenic ester (2 mmol) in 10 mL $CH_2Cl_2$ was added dropwise at $-10^{\circ}C$ over 10 min 0.52 g (2 mmol) of $Ph_3P$ in 3 mL of $CH_2Cl_2$. The reaction mixture was then allowed to warm up to r.t. and was stirred for 24 h. The solvent was

removed under reduced pressure, and the residual solid recrystallized from diethyl ether.

### Trimethyl 3-(1,1,1-Triphenyl-$\lambda^5$-phosphanylidene)-1-propene-1,1,2-tricarboxylate (3a)

Yellow powder; yield: 0.78 g (82%), m.p. 188–189°C. IR (KBr), $\nu_{max}(cm^{-1})$: 1715 (C=O), 1677 (C=O), 1628 (C=O), 1310 (C–O), 1282 (C–O). $^1$H NMR: $\delta = 2.74$ (s, 3H, OMe), 3.59 (s, 6H, OMe), 6.44 (d, $^2J_{PH} =$ 20.0 Hz, 1H, CH), 7.44–7.61 (m, 15H, $C_6H_5$). $^{13}$C NMR: $\delta = 50.1$ (2 OMe), 51.3 (OMe), 66.4 (d, $^1J_{PC} = 108.7$ Hz, CH), 90.8 (d, $^3J_{PC} = 13.7$ Hz, C-1), 124.7 (d, $^1J_{PC} = 91.6$ Hz, $C_{ipso}$), 129.0 (d, $^2J_{PC} = 11.5$ Hz, $C_{ortho}$), 132.8 (d, $^4J_{PC} = 2.0$ Hz, $C_{para}$), 133.5 (d, $^3J_{PC} = 12.5$ Hz, $C_{meta}$), 158.2 (d, $^2J_{PC} =$ 5.0 Hz, C-2), 169.1 (C=O), 170.0 (d, $^3J_{PC} = 8.7$ Hz, C=O). MS (EI, 70 eV): m/z (%) = 476 ($M^+$, 3), 277 (100), 199 (30), 183 (40), 77 (75), 51 (42). Anal. calcd. for $C_{27}H_{25}O_6P$ (476.5): C, 68.06; H, 5.29%. Found: C, 68.15; H, 5.20%.

### Ethyl Dimethyl 3-(1,1,1-Triphenyl-$\lambda^5$-phosphanylidene)-1-propene-1,1,2-tricarboxylate (3b)

Yellow powder; yield: 0.73 g (75%), m.p. 205–207°C. IR (KBr), $\nu_{max}(cm^{-1})$: 1699 (C=O), 1640 (C=O), 1299 (C–O), 1262 (C–O). $^1$H NMR: $\delta = 0.81$ (t, $^3J_{HH} = 6.8$ Hz, 3H, $CH_3$), 3.01 (q, $^3J_{HH} = 6.8$ Hz, 2H, $OCH_2$), 3.58 (s, 6H, OMe), 6.42 (d, $^2J_{PH} = 21.5$ Hz, 1H, CH), 7.44–7.58 (m, 15H, $C_6H_5$). $^{13}$C NMR: $\delta = 13.3$ (Me), 50.5 (OMe), 60.7 ($OCH_2$), 66.5 (d, $^1J_{PC} =$ 104.0 Hz, CH), 91.0 (d, $^3J_{PC} = 11.9$ Hz, C-1), 125.0 (d, $^1J_{PC} = 91.2$ Hz, $C_{ipso}$), 128.9 (d, $^2J_{PC} = 11.4$ Hz, $C_{ortho}$), 132.7 (d, $^4J_{PC} = 2.2$ Hz, $C_{para}$), 133.5 (d, $^3J_{PC} = 12.5$ Hz, $C_{meta}$), 158.4 (d, $^2J_{PC} = 4.8$ Hz, C-2), 169.1 (C=O), 169.7 (d, $^3J_{PC} = 8.7$ Hz, C=O). MS (EI, 70 eV): *m/z* (%) = 489 ($M^+$-1, 5), 417 (10), 262 (100), 303 (5), 183 (70), 108 (35), 77 (20), 57 (60). Anal. calcd. for $C_{28}H_{27}O_6P$ (490.5): C, 68.57; H, 5.55%. Found: C, 68.45; H, 5.26%.

### Tetramethyl 3-(1,1,1-Triphenyl-$\lambda^5$-phosphanylidene)-1-propene-1,1,2,3-tetracarboxylate (3c)

Yellow powder; yield: 0.96 g (90%), m.p. 200–202°C (dec.). IR (KBr), $\nu_{max}(cm^{-1})$: 1732 (C=O), 1686 (C=O), 1653 (C=O), 1246 (C–O), 1207

(C—O). $^1$H NMR: $\delta$ = 3.09 (s, 3H, $OCH_3$), 3.47 (s, 6H, $OCH_3$), 4.06 (s, 3H, $OCH_3$), 7.52–7.63 (m, 15H, $C_6H_5$). $^{13}$C NMR: $\delta$ = 51.0 (OMe), 52.4 (OMe), 52.6 (2 OMe), 71.1 (d, $^1J_{PC}$ = 125.0 Hz, C-3), 87.2 (d, $^3J_{PC}$ = 11.2 Hz, C-1), 122.1 (d, $^1J_{PC}$ = 87.5 Hz, $C_{ipso}$), 129.1 (d,$^2J_{PC}$ = 11.5 Hz, $C_{ortho}$), 133.4 (d, $^4J_{PC}$ = 2.2 Hz, $C_{para}$), 134.3 (d, $^3J_{PC}$ = 12.5 Hz, $C_{meta}$), 160.1 (d, $^2J_{PC}$ = 13.7 Hz, C-2), 164.6 (d, $^3J_{PC}$ = 11.2 Hz, C=O), 167.4 (d, $^2J_{PC}$ = 19.5 Hz, C=O), 168.6 (C=O). MS (EI, 70 eV): m/z (%) = 534 ($M^+$, 5), 517 (10), 262 (20), 183 (70), 111 (35), 69 (60), 57 (60). Anal. calcd. for $C_{29}H_{27}O_8P$ (534.5): C, 65.17; H, 5.09%. Found: C, 65.10; H, 5.14%.

## Diethyl Dimethyl 3-(1,1,1-Triphenyl-$\lambda^5$-phosphanylidene)-1-propene-1,1,2,3-tetracarboxylate (3d)



Yellow powder; yield: 0.91 g (81%), m.p. 218–220°C (dec.). IR (KBr), $\nu_{max}$($cm^{-1}$): 1715 (C=O), 1650 (C=O), 1620 (C=O), 1215 (C—O), 1210 (C—O). $^1$H NMR: $\delta$ = 1.00 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $CH_3$), 1.19 (t, $^3J_{HH}$ = 7.0 Hz, 3H, $CH_3$), 3.62 (s, 6H, OMe), 4.15 (q, $^3J_{HH}$ = 7.2 Hz, 2H, $OCH_2$), 4.22 (q, $^3J_{HH}$ = 7.0 Hz, 2H, $OCH_2$), 7.41–7.59 (m, 15H, $C_6H_5$). $^{13}$C NMR: $\delta$ = 13.9 (Me), 15.9 (Me), 51.8 (2 OMe), 57.2 ($OCH_2$), 59.3 ($OCH_2$), 60.7 (d, $^1J_{PC}$ = 77.1 Hz, C-3), 84.7 (d, $^3J_{PC}$ = 11.2 Hz, C-1), 128.5 (d, $^1J_{PC}$ = 91.2 Hz, $C_{ipso}$), 131.4 (d,$^2J_{PC}$ = 11.5 Hz, $C_{ortho}$), 133.2 (d, $^4J_{PC}$ = 2.3 Hz, $C_{para}$), 134.3 (d, $^3J_{PC}$ = 12.5 Hz, C-2), 162.0 (d, $^2J_{PC}$ = 12.5. Hz, C-2), 166.2 (d, $^3J_{PC}$ = 8.7 Hz, C=O), 167.8 (d, $^2J_{PC}$ = 12.1 Hz, C=O), 171.6 (C=O). MS (EI, 70 eV): m/z (%) = 562 ($M^+$, 5), 517 (10), 262 (20), 183 (70), 111 (35), 71 (60). Anal. calcd. for $C_{31}H_{31}O_8P$ (562.5): C, 66.19; H, 5.55%. Found: C, 66.16; H, 5.47%.

## Di-*tert*-butyl Dimethyl 1-Methoxy-3-(1,1,1-triphenyl-$\lambda^5$-phosphanylidene)-1,1,2,3-propaneteracarboxylate (5)

Colorless crystals; yield: 1.20 g (92%), m.p. 183–184°C. IR (KBr), $\nu_{max}$ ($cm^{-1}$): 1729 (C=O), 1628 (C=O), 1316 (C—O), 1246 (C—O). $^1$H NMR: $\delta$ = 0.85 (s, 9H, C*Me*$_3$), 1.50 (s, 9H, C*Me*$_3$), 3.00 (s, 3H, OMe), 3.15 (d, $^3J_{PH}$ = 18.1 Hz, 1H, CH), 3.57 (s, 3H, OMe), 3.83 (s, 3H, OMe), 7.41–7.57 (m, 15H, $C_6H_5$). $^{13}$C NMR: $\delta$ = 28.2 (C*Me*$_3$), 28.3 (C*Me*$_3$), 35.8 (d, $^1J_{CP}$ = 132.5 Hz, C-3), 51.8 (OMe), 52.4 (OMe), 52.7 (OMe), 54.1 (d, $^2J_{PC}$ = 13.7 Hz, CH), 76.1 (C-1), 79.8 (O*C*Me$_3$), 84.7 (O*C*Me$_3$), 127.8 (d, $^3J_{PC}$ = 12.5 Hz, $C_{meta}$), 129.1 (d, $^1J_{PC}$ = 88.0 Hz, $C_{ipso}$), 131.2 ($C_{para}$), 134.5 (d,$^2J_{PC}$ = 10.7 Hz, $C_{ortho}$), 167.7 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 168.1 (C=O), 169.0 (C=O), 170.9 (d, $^3J_{PC}$ = 10.0 Hz, C=O). MS (EI, 70 eV):

m/z (%) = 651 ($M^+$, 5), 517 (15), 489 (25), 377 (100), 333 (30), 183 (56), 77 (45), 57 (43). Anal. calcd. for $C_{36}H_{43}O_9P$ (650.7): C, 66.45; H, 6.66%. Found: C, 66.58; H, 6.70%.

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