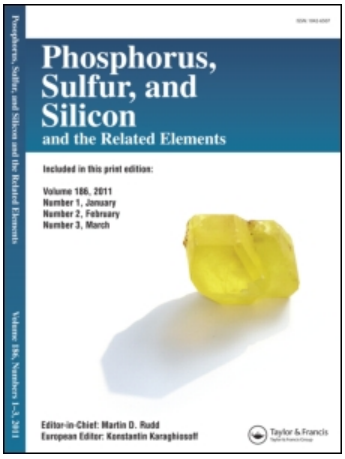

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Three-Component Reaction of Triphenylphosphine, Acetylenic Esters, and Aromatic Amides: The Synthesis of Stable Nitrogen-Containing Phosphorus Ylides

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Three-Component Reaction of Triphenylphosphine, Acetylenic Esters, and Aromatic Amides: The Synthesis of Stable Nitrogen-Containing Phosphorus Ylides

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Protonation of the reactive 1:1 intermediate produced in the reaction between dialkyl acetylenedicarboxylates and triphenylphosphine by aromatic amides leads to vinylphosphonium salts, which undergo a Michael addition with the conjugate base of the amide to produce highly functionalized, salt-free phosphorus ylides in good yields.

Keywords Acetylenic esters; aromatic amides; phosphorus ylides; triphenylphosphine

INTRODUCTION

Phosphorus ylides are reactive systems, which take part in many reactions of value in organic synthesis.[1–7] Several methods have been developed for the preparation of phosphorus ylides. They are usually obtained by treatment of a phosphonium salt with a base; phosphonium salts are usually prepared from the corresponding phosphines and an alkyl halide.[1,2] Phosphonium salts also are prepared by a Michael addition of phosphorus nucleophiles to activated olefins.[1] Phosphonium salts are most often converted to ylides by treatment with a strong base, although weaker bases can be used if the salt is acidic enough. Recently, the reaction of acetylenic esters with triphenylphosphine in the presence of organic N-H acids has been reported to produce nitrogen-containing phosphorus ylides.[8] Here we report an efficient synthetic route to stable phosphorus ylides using triphenylphosphine, aromatic amides, and dimethyl or diethyl acetylenedicarboxylate. Thus, the reaction of amides **1** with acetylenic esters **2** in the presence of

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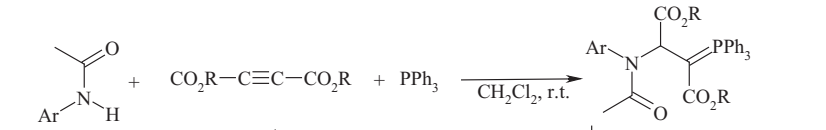
triphenylphosphine leads to the corresponding ylides **3** in good yields (Scheme 1).



1	Ar
a	Phenyl
b	1-Naphthyl

2	R
a	Me
b	Et

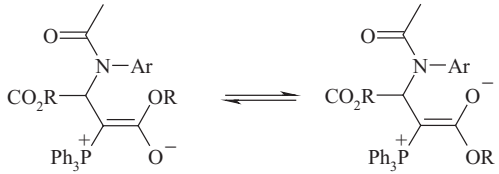
3	Ar	R	Yield (%)
a	Phenyl	Me	95
b	1-Naphthyl	Me	98
c	1-Naphthyl	Et	98

SCHEME 1

RESULTS AND DISCUSSION

Structures of compounds **3a–c** were deduced from their elemental analyses and their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of these ylides are fairly similar and display molecular ion peaks.

NMR spectra of ylides **3a–c** were consistent with the presence of two isomers. The ylide moiety of these compounds was strongly conjugated with the adjacent carbonyl group, and rotation about the partial C,C double bond was slow on the NMR time scale at r.t. (Scheme 2).



SCHEME 2

The ^{1}H NMR spectrum of **3a** displayed 3 sharp lines (δ 1.7, 3.0, and 3.8) for the major isomer arising from the methyl groups, along with a signal for the methine proton at 5.3, which appeared as a doublet ($^{3}J_{PH}$ = 19 Hz). The corresponding signals for the minor isomer appeared at δ 2.2, 2.8, and 3.9 (for the methyl groups) and at δ 5.6 ($^{3}J_{PH}$ = 20 Hz) for the methine proton. The ^{31}P NMR spectrum of compound **3a** consisted of 2 signals at 26.2 and 25.6 for the major and the minor isomer, respectively. These shifts were similar to those observed for other stable phosphorus ylides.[9,10] The structural assignments made on the basis of the NMR spectra of compounds **3a–c** were supported by their

IR spectra. The carbonyl region of the spectrum exhibited absorption bands at 1712–1743 cm^{-1} for the ester groups.

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[1–7] it is reasonable to assume that ylide **3** resulted from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acidic amide. In a second step, the positively-charged ion was attacked by the amide anion to form phosphorane **3**.

In summary, phosphorus ylides may be prepared by a simple, one-pot three-component reaction of acetylenic esters, aromatic amides, 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.

EXPERIMENTAL

All melting points are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-rapid 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 BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz, respectively. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in $CDCl_3$ solution using TMS as internal standard (^{1}H, ^{13}C) or 85% H_3PO_4 as an external standard (^{31}P). Chemicals used in this work were purchased from Fluka (Buchs SG, Switzerland) and were used without further purification.

Synthesis of Phosphorus Ylides 3a–c: General Procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and amide **1** (1 mmol) in dichloromethane (10 mL) was added dropwise a mixture of acetylenic ester **2** (1 mmol) in dichloromethane (5 mL) at r.t. over 10 min. The reaction mixture was then stirred for 2 h. The solvent was removed under reduced pressure, and the solid residue was recrystallized from hexane-ethyl acetate.

Dimethyl 2-Acetylphenylamino-3-triphenylphosphanylidene Butanedioic Acid (3a)

Colorless crystals, m.p. 168–169°C. IR (KBr) $\upsilon(cm^{-1})$: 1743, 1712 (C=O, ester), 1655 (C=O, amide). Elemental analysis: Calcd. for $C_{32}H_{30}NO_5P$: C, 71.23; H, 5.60; N, 2.60%. Found: C, 71.23; H, 5.50; N, 2.74%. MS (m/z, %): 539 (M, 3), 405 (52), 262 (100), 183 (47), 93 (74), 43 (34). Major isomer (65%): ^{1}H NMR ($CDCl_3$): δ 1.71 (s, 3H, CH_3CON),

3.03 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.35 (d, $^3J_{HP} = 19.1$ Hz, 1H, CH), 7.31–7.61 (m, 20H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 23.4 (CH_3CON), 39.2 (d, $^1J_{PC} = 125.0$ Hz, C=P), 49.5 (OCH_3), 52.2 (OCH_3), 61.1 (d, $^2J_{PC} = 17.0$ Hz, CH), 126.9 (CH, C_6H_5), 127.9 (CH, C_6H_5), 131.4 (CH, C_6H_5), 141.3 (C-*i*), 126.3 (d, $^1J_{PC} = 91.0$ Hz), 129.1 ($^2J_{PC} = 12.0$ Hz), 132.4 (d, $^4J_{PC} = 1.0$ Hz), 134.2 (d, $^3J_{PC} = 10.0$ Hz), 170.0 (CO), 173.3 (CO), 173.4 (CO). ^{31}P NMR ($CDCl_3$): δ 26.2. Minor isomer (35%): ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 3H, CH_3CON), 2.83 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 5.42 (d, $^3J_{PH} = 20.0$ Hz, 1H, CH), 7.31–7.61 (m, 20H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 23.1 (CH_3CON), 41.1 (d, $^1J_{PC} = 127.0$ Hz, C=P), 49.0 (OCH_3), 51.9 (OCH_3), 61.9 (d, $^2J_{PC} = 18.0$ Hz, CH), 126.8 (CH, C_6H_5), 127.6 (CH, C_6H_5), 131.2 (CH, C_6H_5), 141.4 (C-*i*), 169.1 (CO), 172.3 (CO), 172.5 (CO). ^{31}P NMR ($CDCl_3$): δ 25.6.

Dimethyl 2-(Acetyl-naphthalene-2-yl-amino)-3-triphenyl-phosphanylidene Butanedioic Acid (3b)

White powder, m.p. 175–176°C. IR (KBr) υ(cm^{-1}): 1751, 1712 (C=O, ester), 1636 (C=O, amide). Elemental analysis: Calcd. for $C_{36}H_{32}NO_5P$: C, 73.33; H, 5.47; N, 2.38%. Found: C, 73.14; H, 5.21; N, 2.41%. MS (m/z, %): 589 (M, 1), 574 (29), 405 (37), 262 (100), 183 (56), 77(23). Major isomer (55%): ^{1}H NMR ($CDCl_3$): δ 1.61 (s, 3H, CH_3CON), 2.60 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 5.63 (d, $^3J_{PH} = 19.0$ Hz, 1H, CH), 7.03–8.30 (m, 22H, C_6H_5 and naphthyl). ^{13}C NMR ($CDCl_3$): δ 23.4 (CH_3CON), 39.0 (d, $^1J_{PC} = 126.0$ Hz, C=P), 48.9 (OCH_3), 52.8 (OCH_3), 61.2 (d, $^2J_{PC} = 18.0$ Hz, CH), 123.9, 125.9, 126.8, 127.9, 128.6, 129.9, 134.3 (CH, naphthyl), 129.5, 132.7, 137.3 (C, naphthyl), 126.3 (d, $^1J_{PC} = 91.0$ Hz), 129.1 (d, $^2J_{PC} = 12.0$ Hz), 132.8 (d, $^4J_{PC} = 1.0$ Hz), 133.5 (d, $^3J_{PC} = 10.0$ Hz), 172.0 (CO), 171.8 (CO), 174.0 (CO). ^{31}P NMR ($CDCl_3$): δ 25.4. Minor isomer (45%): ^{1}H NMR ($CDCl_3$): δ 1.61 (s, 3H, CH_3CON), 3.24 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 5.50 (d, $^3J_{PH} = 20.0$ Hz, 1H, CH), 7.03–8.30 (m, 22H, C_6H_5 and naphthyl). ^{13}C NMR ($CDCl_3$): δ 23.6 (CH_3CON), 40.0 (d, $^1J_{PC} = 127.0$ Hz, C=P), 49.8 (OCH_3), 52.4 (OCH_3), 59.8 (d, $^2J_{PC} = 18.0$ Hz, CH), 124.1, 126.3, 126.6, 127.7, 128.7, 130.0, 134.4 (CH, naphthyl), 129.2, 133.3, 137.5 (C, naphthyl), 126.5 (d, $^1J_{PC} = 91.0$ Hz), 129.1 (d, $^2J_{PC} = 12.0$ Hz), 132.8 (d, $^4J_{PC} = 1.0$ Hz), 134.0 (d, $^3J_{PC} = 10.0$ Hz), 169.0 (CO), 171.3 (CO), 173.1 (CO). ^{31}P NMR ($CDCl_3$): δ 25.7.

Diethyl 2-(Acetyl-naphthalene-2-yl-amino)-3-triphenyl-phosphanylidene Butanedioic Acid (3c)

White powder, m.p. 158–159°C. IR (KBr) υ(cm^{-1}): 1747, 1712 (C=O, ester), 1636 (C=O, amide). Elemental analysis: Calcd. for $C_{38}H_{36}NO_5P$: C, 73.89; H, 5.87; N, 2.27%. Found: C, 73.50; H, 5.82; N, 2.44%.

MS (m/z, %): 617 (M, 1), 612 (11), 433 (57), 262 (100), 183 (45), 77 (32). Major isomer (52%): ^{1}H NMR ($CDCl_3$): δ 0.21 (t, $^{3}J_{HH} = 7.0$ Hz, 3H, CH_3), 1.45 (t, $^{3}J_{HH} = 7.0$ Hz, 3H, CH_3), 1.63 (s, 3H, CH_3CON), 3.10–4.31 (m, 4H, OCH_2), 5.31 (d, $^{3}J_{PH} = 19.0$ Hz, 1H, CH), 7.00–8.42 (m, 22H, C_6H_5 and naphthyl). ^{13}C NMR ($CDCl_3$): δ 14.1 (CH_3), 14.9 (CH_3), 23.3 (CH_3CON), 38.9 (d, $^{1}J_{PC} = 126.0$ Hz, C=P), 57.6 (OCH_2), 61.3 (OCH_2), 61.2 (d, $^{2}J_{PC} = 16.0$ Hz, CH), 124.1, 126.3, 127.2, 127.9, 129.0, 129.9, 132.5 (CH, naphthyl), 129.2, 133.2, 137.4 (C, naphthyl), 126.1 (d, $^{1}J_{PC} = 91.0$ Hz), 129.1 (d, $^{2}J_{PC} = 12.0$ Hz), 132.0 (d, $^{4}J_{PC} = 1.0$ Hz), 134.1 (d, $^{3}J_{PC} = 10.0$ Hz), 171.8 (CO), 173.1 (CO), 173.2 (CO). ^{31}P NMR ($CDCl_3$): δ 25.0. Minor isomer (48%): ^{1}H NMR ($CDCl_3$): δ 1.11 (t, $^{3}J_{HH} = 7.0$ Hz, 3H, CH_3), 1.50 (t, $^{3}J_{HH} = 7.0$ Hz, 3H, CH_3), 1.64 (s, 3H, CH_3CON), 3.40–4.31 (m, 4H, OCH_2), 5.41 (d, $^{3}J_{PH} = 18.0$ Hz, 1H, CH), 7.00–8.42 (m, 22H, C_6H_5 and naphthyl). ^{13}C NMR ($CDCl_3$): δ 14.7 (CH_3), 15.1 (CH_3), 23.5 (CH_3CON), 41.3 (d, $^{1}J_{PC} = 128.0$ Hz, C=P), 58.2 (OCH_2), 61.3 (OCH_2), 60.0 (d, $^{2}J_{PC} = 18.0$ Hz, CH), 124.1, 126.3, 127.2, 127.9, 129.0, 129.9, 132.5 (CH, naphthyl), 129.2, 133.2, 137.4 (C, naphthyl), 126.1 (d, $^{1}J_{PC} = 91.0$ Hz), 129.1 (d, $^{2}J_{PC} = 12.0$ Hz), 132.0 (d, $^{4}J_{PC} = 1.0$ Hz), 134.1 (d, $^{3}J_{PC} = 10.0$ Hz), 169.1 (CO), 171.1 (CO), 172.8 (CO). ^{31}P NMR ($CDCl_3$): δ 26.0.

REFERENCES

[1] D. E. C. Corbridge, *Phosphorus: An Outline of the Chemistry, Biochemistry, and Uses*, 5th ed. (Elsevier, Amsterdam, 1995).

[2] R. Engel, *Synthesis of Carbon-Phosphorus Bonds* (CRC Press, Boca Raton, FL, 1988).

[3] O. I. Kolodiazhnyi, *Russ. Chem. Rev.*, **66,** 225 (1997).

[4] H. J. Bestmann and R. Zimmermann, *Top. Curr. Chem.*, **109,** 85 (1983).

[5] B. E. Maryano and A. B. Reits, *Chem. Rev.*, **89,** 863 (1989).

[6] K. M. Pietrusiewiz and M. Zablocka, *Chem. Rev.*, **94,** 1375 (1994).

[7] R. A. Aitken, H. Herion, A. Janosi, N. Karodia, S. V. Raut, S. Seth, et al., *J. Chem. Soc. Perkin Trans. 1*, 2467 (1994).

[8] I. Yavari, M. T. Maghsoodlou, H. Djahaniani, and N. Hazeri, *J. Chem. Res.* (*S*), 216 (1999).

[9] J. C. Tebby, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, J. C. Verkade and L. D. Quin, Eds., pp 1–60, (VCH, Weinheim, 1987).

[10] E. Vedejs and K. A. J. Snoble, *J. Am. Chem. Soc.*, **95,** 5778 (1973).